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CONTENTS

RAPID ESTIMATION OF BASE-EXCHANGE PROPERTIES OF SOIL[1]

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It is well known that base-exchange reactions of soil involving metal cations are relatively rapid. The hydrogen ions of soil colloids are, however, replaced very slowly and only to a small extent by neutral salts. Since most of our agricultural soils contain hydrogen ions, the rapidity of these exchange reactions varies with the amount of exchangeable hydrogen present.

Previous reference (4) has been made to the rapid determination of base-exchange capacity and exchangeable hydrogen. In nearly all the rapid chemical methods for determining exchangeable cations in soil, acids or mixtures of salts and acids are employed (3, 6). Base-exchange capacity and exchangeable hydrogen are not usually determined by these methods, but merely the approximate amounts of exchangeable metal cations. Such data are usually insufficient to estimate accurately the base-exchange properties of a soil.

The method for the rapid, approximate determination of base-exchange capacity and exchangeable hydrogen, herewith proposed, is based on the results shown in this and other papers (4, 5). In addition to a detailed description of the method, various practical applications are included. A detailed description of the volumetric determination of barium is given.

THE METHOD

The basis for the rapid determination of base-exchange properties of soil is in the use of a well-buffered extracting medium and in the titrametric determination of adsorbed barium and neutralized hydroxyl ions. Both of these determinations are made on one aliquot. The reaction of the buffer is adjusted to pH 8.2, because at this pH value barium adsorption attains a maximum, as shown in table 1 and elsewhere (5). The results of Puri and Uppal (8) also show that the base-exchange capacity is fairly constant above pH 8.0. They determined the base-exchange capacity of several soils by various methods, using neutral salts, hydrolyzed salts, bases, and pretreatment of soils with barium hydroxide and subsequent replacement with neutral or hydrolyzed salts. In all cases the final pH values of the soil after

[1] Contribution from the department of agronomy, North Carolina Agricultural Experiment Station. Published with the approval of the director as Paper No. 129 of the Journal Series.

[2] Associate in agronomy. The writer is indebted to E. G. Moss, R. F. Poole, and E. R. Collins for some of the soil samples and field data reported in table 6.

treatment were measured. Their results, presented in table form, have been plotted in figure 1. The numbers given are the soil numbers of Puri and Uppal as reported in their table 2. Each point refers to the final pH value and base-exchange capacity of a different method. The most important features of these curves are not the direct relationships of base-exchange capacity to pH as stated by the writers, but rather the constancy of base-exchange capacity between pH 8.0 and pH 9.0.

TABLE 1

Influence of reaction on base-exchange capacity and exchangeable hydrogen of soil

SOIL NUMBER	SOIL TYPE	REACTION OF SOIL	REACTION OF BARIUM CHLORIDE-TRIETHANOLAMINE BUFFER								
			pH 8.0			pH 8.2			pH 8.4		
			Base-exchange capacity	Exchangeable hydrogen		Base-exchange capacity	Exchangeable hydrogen		Base-exchange capacity	Exchangeable hydrogen	
		pH	*m e*	*m e.*	*per cent*	*m e*	*m e*	*per cent*	*m e*	*m e.*	*per cent*
100	Muck	5.80	63.8	32.5	51.0	73.5	43.0	58.5	74.4	44.0	59.2
101	Portsmouth fine sandy loam	4.77	16.0	13.7	85.4	17.1	14.8	86.6	17.4	15.2	87.2
Y104	Culvers gravelly silt loam	5.40	12.3	8.0	65.0	17.4	9.6	55.1	17.7	10.6	59.8
120	Memphis sandy loam	4.95	13.0	9.2	70.7	13.4	11.4	85.1	13.8	12.4	89.8
121	Clinton sandy loam	6.80	10.0	3.0	30.5	11.2	5.0	44.6	11.5	5.2	45.3
122	Calcareous soil	7.60	11 4	0.0	0.0	11.9	2.6	21.8	11.6	2.9	25.0
Y226	Culvers gravelly silt loam	5.30	15.4	13.2	85.6	18.1	16.6	91.6	19.2	17.6	91.7
E202	Kalmia fine sandy loam	5.21	4.7	4.0	84.8	5.6	4.7	83.9	5.6	4.5	80.3
D101	Dunbar fine sandy loam	5.80	3.0	2.6	86.5	4.0	2.9	72.4	4.3	3.4	79.2
R104	Cecil clay loam	6.60	3.0	0.9	30.0	4.8	1.6	33.3	4.8	1.8	37.5
E105	Okenee fine sand	4.68	2.6	2.6	100.0	3.5	2.9	83.0	3.6	3.4	94.4
104	Yazoo loam	5.40	12.3	8.0	65.0	17.4	9.6	55.0	17.7	10.6	59.8
Average			13.8	8.1	62.9	16.5	10.4	64.2	16.7	10.8	67.4

At pH 8.2, adsorption of the metal cations is efficient and rapid, requiring only small concentrations of a salt, and permitting the determination of barium adsorbed by the soil by difference. Data given in table 2 show that shaking for only 10 minutes or merely leaching with 50 ml. of the 0.2 *N* barium solution is sufficient to obtain close to maximum base-exchange capacity values and nearly complete replacement of hydrogen. Continuous shaking for 2 hours or intermittent shaking for 20 hours yielded slightly higher values for base-exchange capacity, and particularly for exchangeable hydrogen. The writer ascribes these increases, not to the establishment of a true equilibrium,

but rather to secondary reactions involving, in part, the hydrolysis of the base-exchange complex.

The buffer employed is triethanolamine, which is partly neutralized with hydrochloric acid to obtain the desired pH value. The excellent buffer

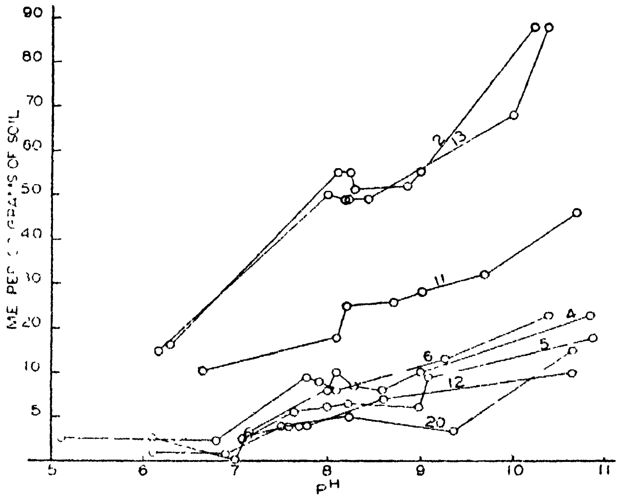

FIG. 1. BASE EXCHANGE CAPACITY OF SOILS IN RELATION TO pH
Data from Puri and Uppal (8)

TABLE 2

Influence of time of shaking on base-exchange capacity and exchangeable hydrogen of soil

SOIL NUMBER	LEACHING METHOD			TIME OF SHAKING: 10 minutes			30 minutes			1 hour			2 hours			20 hours		
	Base-exchange capacity	Exchangeable hydrogen		Base-exchange capacity	Exchangeable hydrogen		Base-exchange capacity	Exchangeable hydrogen		Base-exchange capacity	Exchangeable hydrogen		Base-exchange capacity	Exchangeable hydrogen		Base exchange capacity	Exchangeable hydrogen	
	m.e	*m.e*	*per cent*	*m.e*	*m.e.*	*per cent*	*m.e*	*m.e*	*per cent*	*m.e.*	*m.e*	*per cent*	*m.e.*	*m.e*	*per cent*	*m.e*	*m.e*	*per cent*
100	73.2	41.0	56.0	73.5	43.0	58.5	73.4	42.0	57.2	73.8	43.0	58.2	75.2	46.0	61.2	78.3	52.0	66.4
111	18.4	14.2	77.2	18.8	14.4	76.6	18.5	14.6	78.9	18.4	14.6	79.3	18.8	14.8	78.7	20.0	16.8	84.0
B105	3.3	1.7	51.5	3.4	1.6	47.1	3.4	1.7	50.0	3.6	1.9	52.8	3.7	2.1	56.7	4.0	2.7	67.5
Y222	19.5	17.6	90.3	20.1	18.4	91.5	19.4	16.8	86.6	19.7	18.2	92.4	21.0	20.0	95.2	22.0	21.6	98.2
Y223	16.8	14.3	85.1	16.7	14.9	89.2	17.4	15.2	87.5	16.7	14.4	86.2	18.1	16.0	88.4	20.3	17.6	86.7
Y224	17.5	15.6	89.2	18.0	16.0	88.8	17.4	15.6	89.6	18.7	16.0	85.5	18.2	15.6	85.7	20.7	18.4	89.0
Average	24.8	17.4	70.2	25.1	18.1	72.2	24.9	17.7	71.1	25.2	18.0	71.4	25.8	19.1	74.0	27.5	21.5	78.2

property of triethanolamine has been previously reported (4). In figure 2 the buffer action of triethanolamine against hydrochloric acid is shown. The use of hydrochloric acid for the partial neutralization of triethanolamine has an advantage over acetic acid in that the system is not buffered below pH 5.5

and, therefore, an accurate end point can be obtained in titration through the use of indicators.

The salt used in conjunction with the triethanolamine buffer is barium chloride. Barium is known to be a very efficient ion for the replacement of exchangeable cations in soil. Since barium is found in most agricultural soils only as traces, it involves no analytical difficulties. The tedious gravimetric determination of barium is superseded by the rapid volumetric measurement, in which tetrahydroxyquinone is used as an internal indicator (4). The accuracy of this volumetric method of determining barium is shown in figure 3. The curve represents the actual concentration of barium, and the small circles represent the concentrations of barium as determined volumetrically.

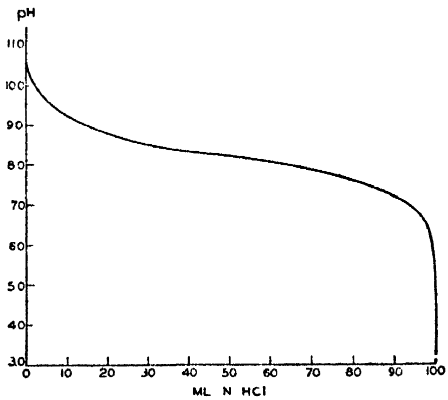

FIG. 2

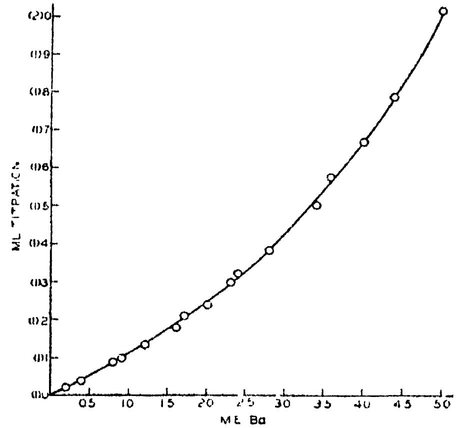

FIG. 3

FIG. 2. INFLUENCE OF ADDITIONS OF N HCl TO 50 ML. 2 N TRIETHANOLAMINE ON pH

FIG. 3. CONCENTRATION OF BARIUM IN SOLUTION (CURVE) AND ITS VOLUMETRIC DETERMINATION, IN WHICH TETRAHYDROXYQUINONE IS THE INDICATOR (CIRCLES)

Preparation and standardization of barium chloride-triethanolamine buffer

For measuring the base-exchange capacity and the exchangeable hydrogen, the following solutions are needed:

Solution A. Barium chloride-triethanolamine, approximately 0.2 N in terms of Ba ions and 0.12 N in terms of OH ions. To prepare this solution dilute 250 ml. of commercial triethanolamine with 9 liters of distilled water, add about 650 ml. of 1:10 HCl to adjust the buffer to pH 8.2, and *then* dissolve 245 gm. of $BaCl_2 \cdot 2H_2O$. This solution does not need to be made up to a definite normality, but it is essential to determine its concentration and prepare a potassium sulfate solution one-half the normality in terms of barium ions, and a hydrochloric acid solution of equal titration value. Protect the solution from the CO_2 of the air.

Solution A_1. Solution A diluted with an equal volume of distilled water. To be used for soils having a low base-exchange capacity, as shown in table 3. Protect the solution from the CO_2 of the air.

Solution B Dissolve 17.5 gm. of dried K_2SO_4 in 2 liters of distilled water Pipette 10 ml. of this solution into a 250- or 300-ml. Erlenmeyer flask, add 10 ml. of distilled water, about 20 ml. of ethyl alcohol, mix and then titrate with solution A_1, using a 5 ml. serological pipette graduated to the tip. After the addition of about 8 ml., add 300 mgm. tetrahydroxyquinone, shake thoroughly after each addition of a few drops and note the change of color of the whole solution from yellow to rose-red. The concentration of solution B is correct when the last drop of the 10-ml aliquot produces a permanent rose-red color.

Solution C. Prepare an approximately 0.12 *N* solution of HCl. Pipette 10 ml. of this solution into an Erlenmeyer flask, add 2 drops of methyl orange and titrate with solution A until the color changes from orange to yellow. The concentration of solution C is correct when the last drop of a 10-ml. aliquot of solution A changes the indicator from orange to yellow.

Solution D. 0.05 *N* barium chloride-triethanolamine. This solution is used to determine the actual amount of barium adsorbed by the soil and the amount of hydrogen neutralized. In place of this solution 0.05 *N* $Ba(OH)_2$ can be used. Barium chloride-triethanolamine is preferable, however, since the CO_2 of the air does not interfere in making the titrations. Solution D is prepared as follows: Weigh out 10.414 gm. of dried $BaCl_2$ and dissolve in 1 liter of distilled water. Dilute 25 ml of commercial triethanolamine in 900 ml. of distilled water, add about 65 ml. of 1:10 HCl to adjust to approximately pH 8.2, and dilute with water until 0.1 *N* by titrating against a definite volume of a known concentration of HCl, using methyl orange as the indicator Finally, mix equal volumes of $BaCl_2$ and triethanolamine to obtain a 0.05 *N* solution.

Procedure for obtaining soil extract

The procedure for obtaining the soil extract, using Berkefeld or Mandler filter cylinders, has been previously described (4). Various other methods of filtering and leaching have been tried. Of these, the following leaching method has been found most satisfactory:

Insert a crucible holder, 32 mm. diameter, into a 100-ml. volumetric flask. Place a filter paper, 20 mm. diameter, in the crucible holder and secure centrally in place by moistening with a few drops of water. Put a weighed quantity of air-dry soil, which has passed through a 2-mm. sieve, into the crucible holder and cover with a thin layer of absorbent cotton or filter paper. Leach with 50 ml. of solution A (or A_1). This may be done by inverting a 50-ml. volumetric flask and holding it in place about 1 cm. above the soil by means of a funnel support. After the solution has passed through the soil, allow about 1 hour for complete drainage. Then refill the 50-ml. flask with distilled water and leach to remove the excess barium. Leach with enough water to just about fill to the mark of the 100-ml. flask. Make up to volume with water and mix the soil extract and leachates very thoroughly. Aliquots of this extract are then used for measuring the base-exchange capacity, exchangeable hydrogen, magnesium, calcium, and ammonium and nitrate nitrogen.

The primary factor determining the amount of soil to be used is its base-exchange capacity. Larger amounts of soils having a low base-exchange capacity are needed in order to avoid low values due to an extreme reduction of the barium concentration of the extracting solution. Experience with many soil types and with a very large number of samples has shown that the

amounts of soil indicated in table 3 give accurate results. From column I it will be seen that with soils having a low base-exchange capacity 50 ml. of solution A_1 is recommended. This solution is only half the strength of the regular barium chloride-triethanolamine buffer and therefore requires a 20-ml. aliquot instead of 10 ml. This doubles the titration values and increases accuracy. The same procedure is recommended for soils high in clay content and low in base-exchange capacity, which filter very slowly. A smaller amount of soil, therefore, expedites the process.

Base-exchange capacity and exchangeable hydrogen of soil

The base-exchange capacity and the exchangeable hydrogen are determined in one aliquot. Pipette 10 or 20 ml. (see table 3) of the soil extract into a 250- or 300-ml. Erlenmeyer flask, add 5 ml. of solution C and 2 drops of methyl orange. Titrate with solution D until indicator is changed from orange to

TABLE 3

Guide to amount of soil, to concentration of solution, and to amount of aliquot to be used for making determinations

Soil Group	I	II	III	IV	V
Approximate base exchange capacity *m.e./100 gm.*	5	5-15	5-15	15-30	30-60
Kind of soil	Sands or sandy loams low in organic matter	Lateritic or kaolinitic types (slow leaching)	Sandy loams, etc.	Silt and clay loams, etc.	Clays and mucks
Amount of soil *gm.*	25	10	20	10	5
Type of solution, 50 ml.	A_1	A_1	A	A	A
Amount of aliquot *ml.*	20	20	10	10	10
Factor to obtain m.e./100 gm. soil	1	2.5	2.5	5	10

yellow. Record this titer and calculate the milliequivalents of hydrogen for 100 gm. soil by using the suitable factor given in table 3. Add 2 drops of about *N* triethanolamine, 10 ml. of solution B, about 20 ml. of alcohol, shake thoroughly and then add approximately 300 mgm. tetrahydroxyquinone by means of a scoop. The addition of triethanolamine is necessary to raise the pH, since the color of tetrahydroxyquinone fades in an acid solution. Continue to titrate with solution D, shaking the flask vigorously after each addition, until the color changes from yellow to permanent rose-red. The total titer multiplied by the suitable factor given in table 3 equals the base-exchange capacity in milliequivalents per 100 gm. of soil.

This titration is more accurate if a 5-ml. sereological pipette, graduated to the tip, is used and the delivery controlled by means of a Neale-Forbes titration assembly. The end-point of the second titration may be more easily observed if at first a somewhat larger amount of tetrahydroxyquinone is added. With a white background and illumination, the visibility of the end

point is best obtained by looking downward at the contents rather than from the side. Each drop will produce a rose-red color which is easily visible, but if the titration is incomplete it will disappear by shaking. The final reading is taken after addition of the last drop which produced visibility of rose-red coloration at the point of contact. The end point observed in this manner is more accurate than the one in the change of the whole solution from yellow to rose-red.

Exchangeable magnesium of soil

In most of the rapid soil tests, comparisons of color and turbidity intensities are made visually. Though these tests are useful, optical instruments give more accurate measurements of intensities. In the colorimetric determination of magnesium and the turbidimetric determinations of calcium and potassium, a Fisher electrophotometer was found to be quite satisfactory, particularly with the aid of suitable filters. For the determination of magnesium and calcium a green filter, Wratten No. 58, and for the determination of potassium a red filter, Wratten No. 25, were used.

The procedure for the determination of magnesium is as follows: Measure an aliquot of the soil extract into a 25-ml. volumetric flask, and if less than 20 ml. is used, make up to about 20 ml. with distilled water. Add 1 ml. of a 0.02 per cent solution of titan yellow (prepared daily by diluting a 0.1 per cent stock solution which is not more than 4 weeks old). Add 1 ml. of 4 N NaOH (low in CO_2), mix, and make up to volume with distilled water. Pour the solution into an optical cell and note the readings within 2 minutes.

The number of milliequivalents of magnesium is then read directly from a calibrated curve or chart of known concentrations of magnesium and is ultimately expressed as milliequivalents per 100 gm. soil. The calibration curve must be established under conditions identical to those in which the unknown was measured. The color intensity is affected by both the barium and sodium hydroxides; hence, both must be present in about the same concentrations in the standard as in the unknown. Solutions should be protected from CO_2 of the air, because ultimately the barium carbonate interferes with the accurate determination of the magnesium. The optical cell may be kept clean by washing frequently in very dilute acetic acid.

Ammonium and nitrate nitrogen of soil

The ammonium replaced by barium and the nitrates soluble in the extract are determined according to the spot-test methods of Morgan (6).

Ammonium nitrogen test. Place 6 drops of the extracting solution in the cavity of a spot plate, add 3 drops of Nessler's reagent; after 1 minute stir with a glass rod and compare the color with standard solutions containing from 2 to 60 p.p.m. ammonium nitrogen or with permanent standards prepared therefrom. The lowest amount of ammonium nitrogen that can be detected by using 25 gm. of soil is 0.2 mgm.

Nitrate nitrogen test. Place 1 drop of the soil extract in a cavity of the spot plate, add 4 drops of diphenylamine reagent; after 2 minutes stir with a glass rod and compare the intensity of the color with standard solutions containing from 2 to 60 p.p.m. nitrate nitrogen. The lowest amount of nitrate nitrogen that can be detected by using 25 gm. of soil is 0.05 mgm.

Exchangeable calcium and potassium of soil

The determination of calcium requires the preliminary quantitative removal of barium. The great solubility differences of the chromates of barium and calcium suggest their separation with sodium chromate.

Add about 400 mgm. of $Na_2CrO_4 \cdot 4H_2O$, by means of a suitable scoop, to a 25-ml. aliquot of the soil extract, and shake thoroughly. The amount of the salt given refers to an aliquot of solution A. If solution A_1 has been used, add half of the above quantities. The precipitate is then removed by filtering. If the barium is precipitated in large test tubes and allowed to settle overnight the required aliquots can be pipetted off without filtration. With this procedure about 82 per cent of the calcium is recoverable. To compensate for this error the calcium used for standardization is added to solution A_1, and after precipitation of the barium the following procedure is used:

Calcium. Add 10 ml. of the filtrate to 10 ml. of a 0.5 per cent solution of ammonium oxalate contained in a 25-ml. volumetric flask. A smaller aliquot is taken if the calcium is very high. Make up to volume with distilled water, mix thoroughly, and after a few minutes pour the turbid solution into an optical cell and measure the concentration of calcium in an electrophotometer. The amount of calcium present is read from the calibration curve, and the results are expressed in milliequivalents per 100 gm. of soil. In the presence of triethanolamine, the calcium oxalate remains uniformly dispersed, thus increasing the accuracy of its measurement turbidimetrically.

Potassium. The concentration of potassium in an aliquot of this extract is usually too low for an accurate estimation. It is preferable to obtain a separate soil extract, using half the concentration of the Morgan solution (6) and the following procedure: To 10 gm. of soil add 40 ml. of this solution, shake for about 15 minutes and filter. Pipette 10 ml. of the filtrate into a flask or vial, and cool to 10°C. or less (1), add 60 mgm. of sodium cobaltinitrite by means of a suitable scoop, dissolve, add 10 ml. of 95 per cent ethyl alcohol which was cooled to 10°C., mix gently, and after a few minutes pour the turbid solution into a cooled optical cell and measure the concentration of potassium in the electrophotometer. The amount of potassium is read from the calibration curve and expressed as milligrams per 100 gm. of soil.

Application of method to calcareous and halomorphic soils

Laboratory studies (4) have shown that sulfates, carbonates, phosphates, and silicates adsorb appreciable amounts of barium. One per cent additions of various salts of these anions to soil have shown no influence on the base-

exchange capacity, except sulfates, which are quantitatively precipitated. The results of 5 per cent additions of calcite, dolomite, and precipitated calcium carbonate to Sumter clay are given in table 4. These materials have not influenced the base-exchange capacity to any appreciable extent. Measureable amounts of calcium and magnesium were brought into solution from dolomite and partially neutralized the exchangeable hydrogen.

From halomorphic soils, or soils to which large amounts of gypsum were added, soluble sulfates and carbonates should first be removed by leaching with water. This is easily accomplished by placing the required amount of

TABLE 4

Influence of 5 per cent additions of calcite, dolomite, and calcium carbonate to Sumter Clay (pH 7.78) on base-exchange capacity and on exchangeable hydrogen, calcium, and magnesium

TREATMENT	FINAL REACTION OF SOIL	BASE-EXCHANGE CAPACITY	EXCHANGEABLE		
			Hydrogen	Calcium	Magnesium
	pH	m e	m e	m e	m e.
None	8.07	16.8	1.6	14.4	0.35
Calcite	8.11	16.7	1.2	14.4	0.36
Dolomite	8.20	16.3	0.8	15 7	0.41
$CaCO_3$	8.14	16.2	1.4	14 8	0.36

TABLE 5

Influence of sulfates and their subsequent removal with different amounts of water on the base-exchange capacity of soils

TREATMENT	AMOUNT OF WATER LEACHED THROUGH	BASE-EXCHANGE CAPACITY			
		Soil D101	Soil K213	Soil E211	Soil 101
	ml	m e	m e	m e	m e
None	0	4.25	5.15	6.15	15.60
0.1 per cent $CaSO_4$	50	4.20	5.10	6 10	15.55
0.2 per cent $CaSO_4$	50	4.25	5.20	6.20	15.60
0.5 per cent Na_2SO_4	100	4.30	5.20	6 30	15.70
1.0 per cent Na_2SO_4	100	4.50	5.40	6.80	16.30

soil in the crucible holder, leaching with water, and then proceeding in the usual way by leaching with barium chloride-triethanolamine.

The influence, upon base-exchange capacity of soils, of additions of calcium and sodium sulfates subsequently removed with different amounts of water is shown in table 5. If desired, the amount of sulfates removed can be easily determined by taking a 25-ml. aliquot of the leachings, adding 20 ml. of alcohol and 150 mgm. of tetrahydroxyquinone, and titrating with 0.05 N $BaCl_2$. The results in table 5 show that with additions of 0.1 and 0.2 per cent $CaSO_4$ sufficient amounts of sulfate have been removed by 50 ml. of water to nullify its influence on the base-exchange capacity. With additions of 0.5 per cent

Na_2SO_4, at least 100 ml. of water is needed, whereas with 1 per cent additions, 100 ml. of water is insufficient.

PRACTICAL APPLICATION

The importance of base-exchange capacity and of hydrogen, calcium, and magnesium saturation of soils in relation to productivity, soil microbiological activity, and chemical and physical properties of soils, is well recognized. By means of the short tests various exchangeable and soluble cations and anions of the soil are approximated. In all these tests, however, no scheme is included for measuring the base-exchange capacity and the exchangeable hydrogen. Bray says that in his test the determination of hydrogen may be of interest in the future.[3] The combined cations may be considered to constitute the base-exchange capacity of soil above pH 7.0. Below pH 7.0, it is essential that the exchangeable hydrogen be taken into account. Correction for this lack of information by determining the pH values of soil is not tenable, since no definite relationship between pH and exchangeable hydrogen exists (5, 7).

The determination of exchangeable calcium of soils P101, P204, and P205 in table 6 would add but little to an explanation of the differences in the yields of peanuts. The pH values provide a clue, but the greatest differences are found in the exchangeable hydrogen and in the base-exchange capacity. The amount of lime to be added in this case is dependent upon the base-exchange capacity and the exchangeable hydrogen rather than the exchangeable calcium.

The determination of pH and exchangeable calcium or magnesium on soils 10, 21, and 30 in table 6 contributes little to an understanding of the efficiency of these soils in decomposing liming materials, which are used as neutralizing agents in fertilizers, as reported by Collins and Speer (2). They found dolomite to be decomposed by these three soils in the following declining order, Portsmouth, Dunbar, and Norfolk. The highest pH values obtained as a result of the addition of neutralizing materials were 5.29 for Portsmouth, 5.51 for Dunbar, and 6.0 for Norfolk. An explanation of these results is found in the base-exchange capacity and the exchangeable hydrogen values. Portsmouth has four times the capacity of Dunbar and five times that of Norfolk to neutralize the liming materials.

The results of the application of this method to a study of the influence of soil erosion on base-exchange capacity are given in table 6. The base-exchange capacity of the virgin soil (Y183, 283) is approximately twice as high as that of the eroded soil (Y182, 282). Differences in reaction and in exchangeable calcium and magnesium are probably the results of the cultivation of the soil from which Y182 and Y282 were taken.

The results with soils lettered "S" show that excess applications of potash have reduced the exchangeable magnesium to a critical level for proper growth of tobacco on a soil having a very low base-exchange capacity. The average

[3] Bray, R. H. 1936. The use of sodium perchlorate as a reagent for extracting the replaceable and water soluble constituents in soils. Ill. Agr. Exp. Sta. Mimeograph Cir.

Mg:Ca ratio of the soils receiving a normal rate of potash was 1:7; that of soils receiving an excess amount of potash (400 pounds K_2SO_4 per acre, just before planting) was 1:24. It appears that the presence of less than 0.1 m.e. magnesium (about 40 pounds MgO per acre) is associated with symptoms of magnesium deficiency.

The results with the soils lettered "A" show an interesting application of this

TABLE 6

Some base-exchange properties of soil in relation to crop response

SOIL NUMBER	REACTION OF SOIL	BASE-EXCHANGE CAPACITY	EXCHANGEABLE Hydrogen		EXCHANGEABLE Magnesium	EXCHANGEABLE Calcium	REMARKS
	pH	*m e*	*m e*	*per cent*	*m e.*	*m e*	
P 101 P 204 P 205 P 304	5.0 5.0 5.8 6.5	7.6 11.3 3.0 2.1	6.4 10.0 1.6 0.5	84.2 88.5 53.2 23.8	.06 .09 .09 .11	1.0 1.1 1.2 1.4	Wickham fine sandy loam, except P304, which is Altavista fine sandy loam. P101 and 204 are from the lower part of a gently sloping field; P205, from the higher part. No peanut crop was obtained where samples P101 and 204 were taken, nearly all shells being empty "pops," whereas good yields were obtained where samples P205 and, particularly, P304 were taken.
S 100 S 101 S 102 S 103	7.0 6.7 6.5 6.3	1.8 2 4 2.6 2.3	0.2 0.8 1.0 0.8	11.1 33.2 38.4 34 8	.06 .19 .18 .05	1.3 1.2 1.4 1.3	Durham sandy loam. Tobacco showed marked magnesium deficiencies on the field from which S100 and 103 were taken, but no magnesium deficiencies on adjacent fields (S101, S102). S100 and S103 received excessive applications of K_2SO_4 before tobacco planting.
T 100 T 103	5.5 5.8	2.5 3.6	1.9 2.3	76.0 63.9	.07 .35	0.4 1.1	Norfolk fine sandy loam. Cotton showed definite symptoms of magnesium deficiency on the field from which T100 was taken, but no deficiency on the field of which T103 is representative.
10	5.18	16.3	12.8	78.5	.54	2.6	Portsmouth fine sandy loam—See text.
21	5.45	4.2	3.2	76.1	.20	1.1	Dunbar very fine sandy loam—See text.
30	5.42	3.2	2.0	62.4	.18	1.0	Norfolk fine sandy loam—See text.

TABLE 6—*Concluded*

SOIL NUMBER	REACTION OF SOIL	BASE-EXCHANGE CAPACITY	EXCHANGEABLE				REMARKS
			Hydrogen		Magnesium	Calcium	
	pH	*m.e.*	*m.e*	*per cent*	*m.e.*	*m.e.*	
Y 182	5.1	10.0	7.2	72.0	.49	2.2	Culvers gravelly silt loam. Y182 and 282 are from cultivated land now in pasture; Y183 and 283 are 100 feet away from virgin soil. Y282 and 283 represent 0–6-inch depth; 182 and 183 represent 2–6-inch depth. Y182 and 282 represent visibly eroded area. All samples taken at the same slope.
Y 282	5 1	10.0	7.6	76.0	.46	1.9	
Y 183	4.7	18.1	17.6	97.2	.18	0 5	
Y 283	4.8	20.8	19.2	92.2	.11	1.2	
A1018	4.5	11.2	10.4	92 8	.79	1.4	A32 Creedmoor coarse sandy loam; A1018, about 250 feet from A32, is a gall spot (yellowish red color). No bacterial wilt of tobacco on A1018, severe wilt on A32.
A 32	4.4	3.2	2.4	75.0	.12	0.6	
E 100	4.9	9.1	8.0	88.0	.18	1.0	Kalmia fine sandy loam. Yield of sunflowers—average dry weight per pot: E100, 8.3 gm., E200 14.2 gm. E200 received 5 m.e. Ca as $CaCO_3$ per 100 gm. soil.
E 200	5.7	9.3	5.2	56.0	.17	3.2	
D 100	5.2	4.2	2.8	66.6	.20	1.3	Dunbar fine sandy loam. Yield of sunflowers—average dry weight per pot D100, 16 3 gm.; D200 18.8 gm D200 received 2 m.e. Ca per 100 gm. soil.
D 200	6.4	3.9	1.0	25.7	.18	2.4	

method to a study of soil factors in relation to soil-borne diseases of plants. R. F. Poole, of this station, has found that *Bacterium solanacearum*, the causal organism of Granville wilt of tobacco, failed to grow on artificial media below about pH 4.8 but remained virile in soil as low as pH 4.1. The soil surrounding the small area from which No. A1018 was taken is heavily infested with the bacterial organism. Sample A32 is representative of this infested soil. The pH values of these soil samples do not differ materially, but, the base-exchange capacity and exchangeable hydrogen values are much greater in No. A1018. It appears, therefore, that within certain limits the exchangeable hydrogen is more important in its influence upon microbiological activity than is pH.

Results of additions of lime on the yields of sunflowers are also shown in table 6. These experiments were conducted in 4-gallon pots in the greenhouse. The amount of lime added was based on the chemical data of soils E100 and D100. E100 received 5 and D100 received 2 m.e. of Ca, as precipitated

$CaCO_3$, per 100 gm. The chemical data of E200 and D200 were obtained at the time the sunflowers were harvested (36 days after the application of lime). The yields reported are the averages from nine pots each. These results show that liming based on the exchangeable hydrogen and with reference to the base-exchange capacity was very satisfactory. By this method, liming needs of sandy soils can be more accurately estimated, and injurious overliming can be avoided. The proper nutritional balance for plants can be quickly ascertained.

SUMMARY

An improved method for the rapid estimation of base-exchange capacity and of exchangeable hydrogen has been described. Exchangeable magnesium, calcium, potassium, and ammonium and nitrate nitrogen in soil are also determined. Triethanolamine, partly neutralized with HCl to about pH 8.2, serves as an excellent buffer. To this buffer, is added $BaCl_2$ which has a concentration of about 0.2 *N*. Soil in 5- to 25-gm. lots is leached with 50 ml. of the barium chloride-triethanolamine buffer and finally washed with about 50 ml. of distilled water. The combined filtrates are made up to a volume of 100 ml. with distilled water and the various soil properties determined in aliquots of this solution. The base-exchange capacity and the exchangeable hydrogen are equivalent to the difference of the barium- and hydroxyl-ion concentrations respectively before and after treatment of the soil. These properties are measured rapidly in one aliquot by back titrating with 0.05 *N* barium chloride-triethanolamine, methyl orange and tetrahydroxyquinone being used as indicators.

The exchangeable magnesium is determined colorimetrically with titan yellow, using an electrophotometer. The ammonium and nitrate nitrogen are determined by the spot-plate method. The exchangeable calcium and potassium are determined turbidimetrically as the oxalate and cobaltinitrite, respectively, using an electrophotometer. For the determination of calcium the barium is first removed with sodium chromate by a simple and rapid procedure.

Results with various soils showing the possible application of this method to problems of soil fertility, liming, soil erosion, and soil-borne plant diseases are given. The importance of base-exchange capacity and exchangeable hydrogen in connection with these problems is stressed.

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A RAPID VERSUS A QUANTITATIVE METHOD FOR DETERMINING AVAILABLE MAGNESIUM IN SOILS[1]

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In conducting a chemical and vegetative study of available magnesium in Pennsylvania soils,[3] a rapid method for estimating magnesium was compared with a generally accepted quantitative method in order to ascertain the reliability of the rapid method on widely different soils.

This comparison employed the extraction technique characteristic of each method. Had a comparison of the chemical methods alone been desired, only one extraction of each sample would have been necessary, and magnesium could have been determined in this extract by both methods. Since in this study it was desired to evaluate the rapid method in its entirety it was necessary to use two samples of each soil, one for the rapid extraction and determination and the other for the quantitative extraction and determination.

One hundred seventy soil samples were selected in such manner as to represent a wide variation in past agricultural history, in pH, in organic matter content, and in geological origin.

EXPERIMENTAL METHODS

Rapid method

To a 10-gm. sample of air-dry soil, 25 ml. of 0.25 N sodium acetate (pH 5.0) was added, stirred well, let stand about 20 minutes, and decanted through a 15-cm. Whatman #1 filter into a 125-ml. Erlenmeyer flask. This was repeated with 25 ml. more of the extractant, and after the solution had drained from the filter, the soil was stirred from the bottom of the beaker and rapidly transferred to the filter to stand until drainage was complete. This gave a soil-extractant ratio of 1 to 5. For the estimation of magnesium, 5-ml. aliquots were placed in 80- × 25-mm. vials, 10 drops of titian yellow (0.15 gm. in 75 ml. of 75 per cent by volume ethyl alcohol) were added, the vials were shaken, 2.5 ml. of 15 per cent NaOH was added, and the shaking was repeated

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[3] Garman, W. H. Chemical and vegetative studies of magnesium availability in certain Pennsylvania soils. Dissertation, The Pennsylvania State College, 1939. The phase referred to is as yet unpublished.

until mixing in each vial was complete. In about 5 minutes the color developed was compared with that of similarly treated standard magnesium solutions. The standards were made up in the same sodium acetate as that used for extraction, $MgCl_2 \cdot 6H_2O$ being used in concentrations of 1, 4, 8, 12, 16, and 20 p.p.m.

Quantivative method

To a 25-gm. sample of soil in a beaker, 75 ml. of 0.25 *N* sodium acetate (pH 5.0) was added, stirred well, allowed to stand 20 minutes, and then decanted on a wet Whatman #1 filter paper. To the soil remaining in the beaker 50 ml. more of the sodium acetate was added, allowed to stand 15 to 20 minutes, and then decanted through the filter as before. The procedure was repeated with the same quantity of the extractant. When this had drained from the filter, the soil in the beaker was stirred, quickly transferred to the filter, and allowed to drain free of the extractant, after which 25 ml. more was added and allowed to leach through the soil. This gave a soil-extractant ratio of 1 to 8.

Organic matter, manganese, phosphorus, and iron and aluminum were removed from the extracts according to the method of Alexander and Harper.[4] Calcium was precipitated as the oxalate in slightly acid solution, filtered, and titrated with permanganate in the usual manner.

The filtrate from the calcium was evaporated to about 75 ml., 25 ml. of nitric acid added, evaporated to dryness on a steam bath, and then heated 20 to 30 minutes on a hot plate to drive off the oxalate. Upon cooling, the residue was taken up with 5 ml. of HCl, evaporated almost to dryness, and the suspended material dissolved by adding 75 ml. of water and 3 ml. more of HCl with stirring. After the solution stood a few minutes, 5 ml. of 10 per cent potassium citrate was added, followed by 5 to 8 ml. of 10 per cent $(NH_4)_2HPO_4$, and this made slightly alkaline to phenolphthalein by means of (1 + 2) NH_4OH. The solution was then stirred vigorously with a rubber policeman, the sides and bottom of the beaker (150 ml.) being rubbed until the NH_4MgPO_4 precipitate was well formed. After the beaker stood 10 to 15 minutes, 10 ml. of concentrated ammonia was added with stirring and the beaker was covered and left standing overnight.

The precipitate was filtered under suction through a Gooch crucible containing a carefully cut and well-fitted circle of Whatman #44 filter paper. The beaker and the precipitate in the crucible were washed 6 to 8 times with 2 per cent NH_4OH, care being taken that the sides of the crucible were washed clean each time. Air was then drawn through for about 5 minutes, the crucible placed on its side and allowed to dry for at least 6 hours. The magne-

[4] Alexander, G., and Harper, H. J. 1936 Procedure for the determination of exchangeable magnesium in soil. Mimeographed.

sium was finally determined by dissolving the precipitate in 20 ml. of 0.1 N H_2SO_4 and titrating with 0.1 N NaOH.

RESULTS AND DISCUSSION

In addition to the results expressed in pounds per acre of magnesium by the rapid and quantitative methods, the percentages of organic matter and the pH values are given in table 1 for most of the soils.[5]

In figure 1 the results of the magnesium determinations by the two methods are plotted. From this diagram pattern it at once seems apparent that in specific instances there is considerable disagreement between the methods. Despite this seemingly high degree of digression, especially in the higher ranges, these data are characterized by a remarkably high coefficient of correlation, r being 0.80. Furthermore, this coefficient denotes a high degree of significance, inasmuch as it has a standard error of $\pm$ 0.03, and in addition has a t value (Fisher's method) of 17.4, which greatly exceeds that necessary (2.58) for a probability of 0.01.

Table 2 affords a further comparison of the two methods. Here the data of both methods are arranged into uniform classes, 0 to 49, 50 to 99, etc., pounds per acre of extractable magnesium. Also, the number of samples falling into each class, and the percentage of the total in each class, are given, as well as the accumulative percentages. It should be noted that this table includes all 170 samples by the quantitative procedure, and 169 samples by the rapid. (One sample, No. 1451, exceeded the highest class, 400 to 499 pounds per acre by the rapid method.)

Table 2 reveals that these methods agree fairly well in arranging the data into given uniform classes. This agreement appears to be better below the 200-pound-per-acre level than above. This may be due to two factors: first, only about 20 per cent (34 samples) of the 170 samples contained 200 or more pounds per acre of available magnesium, which is too small a number of such data to expect to conform to uniform classing as herein carried out; and second, as already referred to, the two methods are actually subject to greater digression at the higher levels of magnesium. That the latter is true for most soils can be observed by merely examining figure 1. Further light is thrown upon this matter by calculating the coefficients of correlation for the samples below 200 pounds per acre, and for those of that level and above. For the samples with less than 200 pounds per acre of available magnesium, r is 0.87 $\pm$ 0.02[6]; whereas, for the data above that level r is 0.54 $\pm$ 0.09. It should, of course, be kept in mind that the latter is derived from the aforementioned 34 sets of data, a number too small to afford a highly significant correlation;

[5] The authors are indebted to E. C. Dunkle and to Nelson Shaulis for certain of the pH and organic matter determinations reported herein, and as well for aid in collecting many of these samples.

[6] Standard error.

TABLE 1

Magnesium, in pounds per acre, determined in widely varied soils by rapid and by quantitative methods

LABORATORY NUMBER	MAGNESIUM		pH	ORGANIC MATTER
	Quantitative method	Rapid method		
				per cent
2460	238	180	6.9	3.7
2491	139	150	5.3	1.9
2492	11	10	4.7	1.1
2518	94	80	5.0	1.3
2550	168	350	7.6	3.5
2464	53	50	4.8	1.7
2569	24	40	4.7	5.2
2586	115	50	5.0	4.6
2601	84	60	4.6	3.5
2603	55	50	4.7	4.0
2759	65	80	6.9	1.4
2744	348	300	7.3	1.8
2742	71	50	6.0	4.6
2757	55	50	6.6	1.5
2753	146	200	6.9	1.3
2768	83	100	6.2	2.1
2755	199	150	6.5	2.9
2770	192	150	6.4	2.2
2751	110	100	6.3	1.9
2766	345	350	6.7	1.1
2745	60	50	6.2	2.7
2760	146	100	6.9	1.4
2947	377	440	7.0	
2948	302	400	6.7	
2953	139	120	6.3	
2957	77	50	5.5	
2959	125	90	6.0	
2963	98	40	5.3	
2966	293	300	6.6	
2970	305	300	7.3	
2971	379	350	6.5	
2972	274	200	5.8	
2973	213	200	6.2	
2974	257	350	6.5	
3355	41	30	4.5	

TABLE 1—*Continued*

LABORATORY NUMBER	MAGNESIUM		pH	ORGANIC MATTER
	Quantitative method	Rapid method		
				per cent
3356	74	80	5.6	
2969	144	100	6.2	
2802	60	100	4.5	
2803	74	120	7.1	
2998	84	150	7.2	
2999	31	50	6.3	
3000	101	150	6.6	
3001	50	30	5.2	
3002	134	180	6.6	
3003	55	30	5.1	
3004	118	120	5.6	
3005	139	150	5.0	
2800	62	50	5.8	
2801	60	50	5.2	
3513	156	150	5.7	1.2
3316	206	200	6.2	1.5
3317	237	200	6.1	1.9
3318	314	180	5.6	2.2
3319	20	tr.	4.6	1.4
3320	20	10	4.6	1.7
3321	20	10	4.5	2.5
3322	225	200	6.3	1.5
3323	262	180	6.0	2.0
3324	206	200	7.1	1.8
3325	338	200	5.9	1.8
3326	250	250	7.1	1.8
2782	134	180	6.5	
2783	113	180	6.5	
2784	62	60	5.6	
2785	48	100	5.1	
2786	54	80	6.4	
2787	41	60	6.1	
2788	127	200	6.0	
2789	139	250	5.7	
2790	60	100	5.2	
2791	43	60	4.9	
2792	6	10	4.5	
2793	7	10	4.8	
2794	50	100	5.4	
2795	45	80	5.6	

TABLE 1—*Continued*

LABORATORY NUMBER	MAGNESIUM		pH	ORGANIC MATTER
	Quantitative method	Rapid method		
				per cent
2796	41	30	4.9	
2797	50	70	4.7	
2798	43	20	4.6	
2799	43	20	4.8	
3077	74	100	4.6	
3078	65	100	4.6	
3094	84	100	5.3	
3095	65	100	4.6	
3100	22	30	4.4	
3101	31	50	4.6	
3126	103	100	5.3	
3128	113	100	5.1	
3131	144	100	6.0	
3133	400	200	4 8	
3143	31	50	4.5	
3145	22	30	4.3	
3149	227	180	4.7	
3151	319	200	4.6	
4385	158	100	6 4	2.4
4386	178	100	6.5	2.0
4387	178	100	7.6	2.1
4388	151	100	6.1	2.9
4384	127	50	6 1	2.1
3621	41	30	4.4	2.4
3622	89	100	5.4	2.9
3623	341	200	5.8	3.7
3624	12	20	5.5	2.6
3625	194	150	6.3	3.4
3626	154	160	6.0	3.7
3627	62	80	7.5	7.1
3628	41	80	5.8	1.4
3629	10	10	4 4	1.1
3630	101	120	4.5	4.8
1453	130	100	5.5	2.0
1454	82	80	5.9	2.3
1457	151	100	7.0	2.1
1458	38	50	4.8	1.3
1450	348	150	5.9	1.1
1451	466	600	7.8	1.3
1465	170	100	5.5	1.2

TABLE 1—*Continued*

LABORATORY NUMBER	MAGNESIUM		pH	ORGANIC MATTER
	Quantitative method	Rapid method		
				per cent
1466	161	120	6.1	1.1
1467	101	80	6.1	1.4
1470	161	150	6.2	1.2
1487	264	400	6.1	1.1
1495	72	100	4.7	0.66
1496	120	100	5.2	1.8
1497	132	250	4.7	0.53
1508	38	50	5.9	2.0
1509	26	50	6.3	1.8
1510	26	50	5.7	2.1
1511	26	30	5.2	2.1
1585	72	50	4.9	0.64
1586	161	100	5.2	2.7
1589	161	200	6.1	3.9
1590	110	150	5.2	1.3
1591	101	50	4.6	1.9
1593	48	30	6 0	1 6
1594	72	30	5.6	1.6
1596	62	40	4.4	1 3
1597	48	30	5.5	1.6
1599	48	30	5.7	1.5
1602	38	10	4.5	0.84
1610	151	250	6.3	3.6
1611	132	200	6.1	0.77
1619	72	100	7.2	1.5
1620	151	300	6.2	4.4
1621	132	200	6 0	2.0
1648	48	50	4.8	0.33
1652	110	150	7.1	2.2
1653	82	100	4.9	0.49
1657	110	50	5.7	2.2
1658	120	150	5.5	0.62
1660	132	150	4.8	2.70
1661	82	50	4.5	3.4
1662	48	30	5 0	1.5
1663	151	80	5.7	4.3
1664	101	80	4.7	0.47
1665	62	30	5.5	1.9
1668	72	30	4.9	2.8
1674	91	50	6.0	2.5

TABLE 1—*Concluded*

LABORATORY NUMBER	MAGNESIUM		pH	ORGANIC MATTER
	Quantitative method	Rapid method		
				per cent
1622	110	250	6.3	0.5
1624	228	400	7.5	2.1
1625	120	250	7.0	0.7
1626	298	250	6.3	1.7
1627	269	300	7.0	0.62
1629	278	350	6.9	2.0
1631	259	150	6.9	2.6
1636	218	150	7.2	2.0
1637	209	200	6.3	0.79
1639	269	250	6.9	0.78
1638	209	200	5 7	1.4
1642	132	400	7.6	0.50
1645	62	100	7.4	1.8
1646	82	100	4.7	0.39
1647	48	80	6.8	1.4

nevertheless, it can still safely be said that the methods agree better for lower levels of magnesium than for higher levels. This has been further borne out by subsequent experiences of the authors.

The most probable cause of the wider disagreement of the methods at the higher magnesium contents is perhaps the presence of the relatively large amounts of active calcium usually present in most soils of medium to high magnesium content. In these cases large amounts of calcium precipitate in the alkaline solution. The surfaces of the flaky-appearing particles tend to absorb the dye from the solution phase, thus interfering with the color comparison. This phenomenon is generally much more pronounced in soils of high pH and high active calcium, though it is encountered in certain instances where both pH and active calcium are low.

Attempts were made to eliminate the interference of calcium. This was done by precipitating the calcium as the oxalate, centrifuging, and determining magnesium in the usual manner. In numerous cases this removal of calcium improved the accuracy of the test, whereas in certain others it produced little or no difference. The explanation for this is not forthcoming at this time. It can be stated that at times a small amount of precipitate developed in the standards of higher concentrations. The interference, therefore, is due, at least in part, to the precipitation of magnesium hydroxide, and in soils high in active calcium, is aggravated by the precipitation of calcium hydroxide.

The question to be decided is whether the rapid test for magnesium is sufficiently accurate to be of value. If we consider the purpose for which its

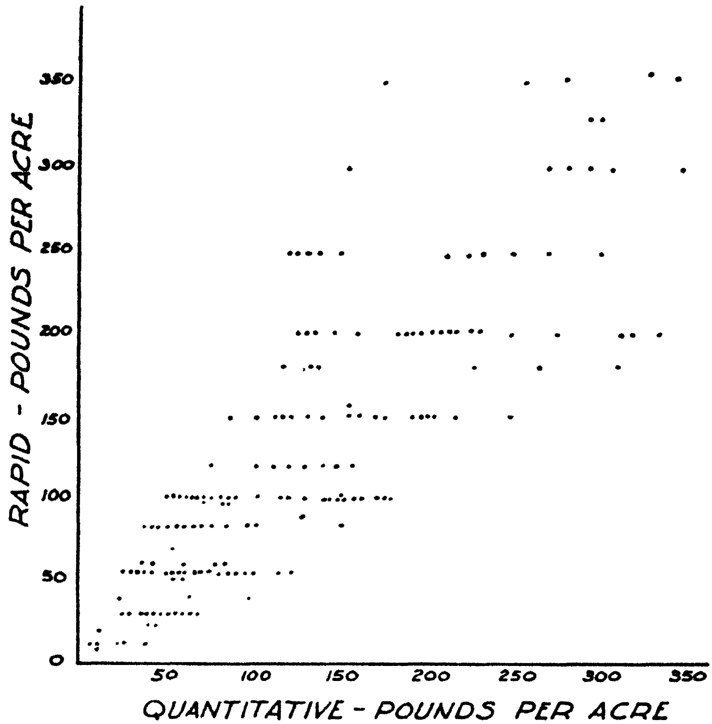

FIG. 1. MAGNESIUM CONTENTS OF WIDELY VARIED SOILS DETERMINED BY RAPID VS. QUANTITATIVE METHOD

TABLE 2

Numbers and percentages of magnesium determinations by rapid and quantitative methods falling within uniform classes

CLASS	RAPID METHOD		QUANTITATIVE METHOD		ACCUMULATIVE PERCENTAGE	
	Number	Per cent	Number	Per cent	Rapid	Quantitative
lbs/acre						
0 to 49	32	18.8	39	22.9	18.8	22.9
50 to 99	37	21.7	40	23.5	40.5	46.4
100 to 149	36	21.2	36	21.2	61.7	67.6
150 to 199	25	14.7	21	12.4	76.4	80.0
200 to 249	16	9.4	10	5.9	85.8	85.9
250 to 299	8	4.7	11	6.4	90.5	92.3
300 to 349	5	2.9	9	5.3	93.4	97.6
350 to 399	5	2.9	2	1.2	96.3	98.8
400 to 499	5	2.9	2	1.2	99.2	100.0

results are commonly utilized, or should be utilized, we readily realize that the data need not be of absolute quantitative accuracy. This is especially true, inasmuch as at this time we are not in a position to say with any degree of cer-

tainty just what level of magnesium is high or low, or what level is sufficient for a given plant on a given soil. In some cases 60 pounds per acre[7] has been regarded as a minimum for certain plants, though these same plants apparently grow normally in certain Pennsylvania soils containing less magnesium. From vegetative work conducted by the authors there is general indication that some degree of plant response to applied magnesium is likely where the extractable magnesium is less than 50 pounds per acre.

If the data in tables 1 and 2 are examined closely, it can be seen that the rapid method separates soils of high magnesium content from those of low content. In a quantitative chemical study of available magnesium in over 200 soil samples from various parts of Pennsylvania it was found that the ordinary agricultural soil may be expected to contain from 40 to 70 pounds per acre, as low, to 150 to 200, as high, numerous soils being both lower and higher, depending largely upon the nature of the soil and the past agricultural history. It is obvious that the rapid method herein described will distinguish a sample with 40 to 70 pounds per acre from one with 150 to 200 pounds.

In prescribing fertilizer recommendations, what we need most is a tool to detect soils of low to very low magnesium content. This method will certainly do this, and in addition may be expected to divide soils reasonably well into smaller groups, as shown in table 2. In routine testing work there is little necessity for dividing soils into more than four groups; namely, low to very low, medium, high, and very high. These findings show that the rapid method will certainly do this. Such a degree of usefulness falls in line with other present-day rapid tests, being probably somewhat more accurate than our potash tests and a little less dependable than our calcium, aluminum, and perhaps phosphorus tests (based on the authors' experience with these methods).

SUMMARY AND CONCLUSION

Available magnesium was determined on 170 selected soil samples by a rapid and by a quantitative procedure, for the purpose of comparing the accuracy of the former with that of the latter on widely different soils.

The coefficient of correlation was 0.80 ± 0.03. For the 136 samples with less than 200 pounds per acre, r was 0.87 ± 0.02, and for the 34 samples with 200 pounds or more per acre, r was 0.54 ± 0.09.

It was shown that the rapid method is fairly reliable in dividing soils into various levels of magnesium content and is sufficiently accurate to meet the needs for which rapid-test data are intended. In the hands of a dependable and experienced worker, it can be relied upon to divide soils into at least four groups as follows: low to very low, medium, high, and very high.

[7] Haddock, J. L. Study of methods for determination of magnesium deficiency in soils. Thesis, Massachusetts State College, 1932. Unpublished.

This method was pointed out as being similar in accuracy to certain other of the common rapid tests in use today, and under ordinary agricultural conditions it should adequately serve the purpose of making soil diagnoses for fertilizer recommendations, where the chief necessity is to detect soils of low to very low available magnesium.

Finally, the use of this method at present seems to be well within the range of chemical accuracy required to coincide with our knowledge as to availability, uptake, and need for magnesium.

A WET COMBUSTION METHOD FOR DETERMINING TOTAL CARBON IN SOILS

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As early as 1848 Rogers and Rogers (10) suggested the use of a chromic-sulfuric acid mixture for the wet oxidation of organic substances. They obtained results on graphite and lamp black which agreed well with dry combustion data. Warrington and Peake (15), in 1880, and Cameron and Breazeale (5), in 1904, applied the wet combustion method to the determination of carbon in soils, but their results were low. Ames and Gaither (3) were the first to show that complete oxidation of soil carbon could be obtained by a chromic-sulfuric acid solution.

Rapid titration methods such as the Schollenberger (11), Walkley and Black (13), and Tiurin (12) do not give complete oxidation of the carbon and therefore require a factor. The use of this factor may introduce an error, as the organic matter in different soils, or even in different horizons of a soil profile, is not always oxidized to the same degree. Crowther (7), in his report on results from a number of wet combustion methods made by different investigators, comments on the large correction factors that were needed (with one exception) and the wide variation when the factors were used. He points out that it is necessary to determine these factors from time to time on soils similar to those being investigated. Because of the difficulty with factors, many workers have avoided rapid titration methods.

Several wet combustion methods have been described which liberate and measure all the carbon present in the soil. Adams (1) determined the total amount of carbon by means of a fairly simple, easily made apparatus in which the CO_2 evolved was caught in a sodium hydroxide tower. The time required for a determination was 40 minutes to 1 hour. Recently, Alper (2) used an evacuated absorption flask instead of the tower, in order to avoid the incomplete absorption of CO_2 which frequently occurs in the tower if the process is carried out rapidly. Alper's procedure is more complicated than Adams', but both give results that agree closely with the dry combustion method.

The method proposed herein, which uses simple apparatus and oxidizes the carbon by $K_2Cr_2O_7$ in H_2SO_4 and H_3PO_4, determines the total carbon present without the use of any factor, and also requires considerably less time than other CO_2 absorption methods.

APPARATUS

The apparatus is shown in figure 1. Two 6-inch absorption towers *A* are filled with ascarite held in place by loose plugs of cotton. These towers are connected to the second dropping funnel *C* by rubber tubing. Addition of the acid through dropping funnel *B* eliminates the removal of the rubber stopper in *C* and thus gives no opportunity for the stopper to come in contact with the sulfuric-phosphoric acid solution. The stem of *C* is bent at an angle of about 30° and is long enough to reach the bottom of the digestion flask *D*. This is a

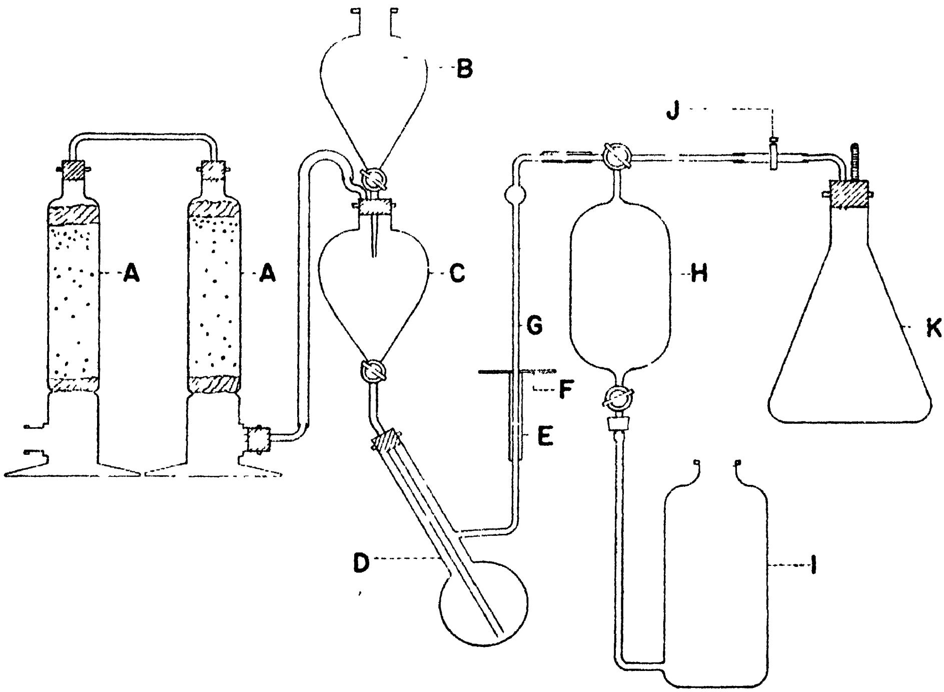

FIG. 1. A, A. Ascarite towers. B, C. Dropping funnels. D. Digestion flask, 50 ml. E. Heavy walled rubber tubing. F. Asbestos shield 3″ square. G. Connecting glass tube and bulb. H. Reservoir, 200 ml. I. Leveling bottle, 250 ml. J. Screw clamp. K. Absorption flask, 500 ml. Erlenmeyer.

50-ml. side-arm distilling flask, which can be heated with a semimicroburner, and is tipped at such an angle that the condensate in tube *G* will drain back into the flask. The side arm, bent through an angle of approximately 75°, is connected to the heavy-walled rubber tube *E* and made air-tight by placing a copper wire tourniquet on *E*. This allows flask *D* to be shaken gently when necessary. In place of the usual water-cooled jacket, an asbestos sheet *F* about 3 inches square is allowed to rest on *E* in order to deflect the heat from the burner and prevent overheating of tube *G*. A small bulb in *G* is necessary to prevent water from being carried into the reservoir. Reservoir *H* is con-

nected to G and K by means of short pieces of rubber tubing. A glass-to-glass connection inside the rubber tubes connecting G to H and D is desirable. The reservoir has a three-way stopcock at the top (which is at first turned to open G to H), and a two-way stopcock at the bottom, and is joined to the leveling bottle I by means of rubber tubing. The capacity of reservoir H is about 200 ml. and that of leveling bottle I about 250 ml. The reservoir is filled with a confining liquid of 3:1 glycerine-water solution containing about 2 gm. of KI per 100 ml. A small excess of the liquid is in the leveling bottle. Absorption flask K is a 500-ml. Erlenmeyer flask fitted with a two-hole rubber stopper. Through one hole is placed a glass tube which is connected to H. A glass plug closes the second hole, but is replaced by an ascarite tube or by the tip of a burette as required. Screw clamp J is used to hold a vacuum in K while it is being connected to the reservoir.

The stopcocks in the two dropping funnels B and C are lubricated with the H_2SO_4-H_3PO_4 solution and those in reservoir H with glycerine. The stopcock in C remains open. The upper stopcock in H is always turned to connect H and D, except at the transfer of gas to K. The stopcock in B is open only when adding acid to the digestion flask.

PROCEDURE

An air-dry soil sample containing 10 to 30 mgm. of carbon (usually 0.5 to 2.0 gm. of soil) is placed in digestion flask D. Powdered $K_2Cr_2O_7$, 1 to 2 gm., is added and the two solids are washed into the bottom of the flask with 3 ml. of distilled water.

The digestion flask is connected to the apparatus and 25 ml. of an acid mixture (60 ml. of concentrated H_2SO_4 and 40 ml. of 85 per cent H_3PO_4) is added to dropping funnel B. The stopcock in B is opened and the acid drawn into the digestion flask by opening the lower stopcock in H and allowing the confining liquid to drain slowly from the reservoir into the leveling bottle. The stopcock in B is then closed.

Heat is applied rather rapidly to the contents of the digestion flask and the lower stopcock in H is adjusted so that CO_2-free air from the ascarite towers is sucked through the digestion mixture at the rate of two bubbles a second. The contents of the flask are shaken for 1 to 2 minutes during the initial vigorous action. Strong heating is continued until the digestion mixture begins to froth, and this temperature is maintained until approximately 25 ml. of glycerine solution remains in the reservoir. The source of heat is then removed and air is sucked through the system until the glycerine is all but drained from the reservoir. The lower stopcock in H is then closed.

Before the absorption flask K is attached to the apparatus, approximately 5 ml. of acetone is added and the flask (including the screw clamp J) is connected to a water aspirator at J. A $CaCl_2$ tube (filled with ascarite held in place by loose cotton plugs) is inserted in the stopper, and a slow current of CO_2-free air is drawn through the flask for about 5 minutes. The suction is stopped,

the $CaCl_2$ tube removed, and in its place the $Ba(OH)_2$ burette inserted so that the tip protrudes below the stopper. Fifty milliliters of standard $Ba(OH)_2$, approximately 0.2 *N*, is added and the glass plug is placed in the hole. Flask *K* is now evacuated by the water pump until the acetone-$Ba(OH)_2$ solution boils vigorously; screw clamp *J* is then closed. To conserve time, the charging and evacuation of the absorption flask may be carried out during the first part of the digestion.

The evacuated Erlenmeyer *K* is joined to the reservoir at *J*. The upper stopcock in *H* is turned to connect *H* and *K*, screw clamp *J* opened, and the lower stopcock in *H* turned to allow the confining liquid to be drawn into the reservoir. When the reservoir is almost filled with the glycerine solution the lower stopcock is closed, screw clamp *J* closed, and the upper stopcock turned to connect the digestion flask and the reservoir. Heat is applied as before and air drawn in by lowering the glycerine in *H*. The system is swept with the CO_2-free air at the rate of 4 to 6 bubbles a second until the reservoir is once more almost filled with gas. The gas is transferred to the absorption flask in the manner already described. After the reservoir has been completely filled with the confining liquid the absorption flask is brought to room pressure by slowly turning the upper stopcock in *H* to connect *H* with digestion flask *D*. To ensure complete absorption of the CO_2, screw clamp *J* is closed and flask *K* shaken. Clamp *J* is then opened and, if CO_2 was present, air will be seen to bubble through the digestion mixture, in which case the process is repeated. The absorption flask is then disconnected at *J*. The glass plug is removed, 4 or 5 drops of thymol blue indicator (0.2 per cent solution in 50 per cent alcohol) added by means of a medicine dropper, and the tip of the acid burette inserted. The excess $Ba(OH)_2$ is titrated with standard 0.2 *N* HCl until the color changes from blue to yellow. The entire procedure, including the weighing of the sample and the titration, requires about 25 minutes. It is not necessary to sweep the apparatus with CO_2-free air before making a determination, as the volume of the apparatus is small and a blank run is made. For soils, a well-ignited noncalcareous soil is used in determining the blank.

Notes on Procedure

A combustion unit may be introduced between the digestion flask and the reservoir. On several soils and on coal a CuO combustion tube was used but did not increase the CO_2 to an appreciable extent. Alper (2) investigated the volatile carbon compounds formed from soils by chromicsulfuric acid oxidation. Soils were run with and without a combustion unit in the train and differences were only 6 parts in 1000. Alper recommended that the combustion tube be omitted unless unusual accuracy was required. In the experiments reported in this paper the unit was not included in the setup.

Chromic acid decomposes when boiled with concentrated H_2SO_4. The H_2SO_4 becomes the oxidizing agent, liberating SO_2, which reacts with the $Ba(OH)_2$. Alper (2) corrected for the $BaSO_3$ formed by oxidizing it to $BaSO_4$ with H_2O_2, but this meant an extra step in the procedure and a double titration. It was found that a 60:40 solution of H_2SO_4 and H_3PO_4 prevented the formation of the SO_2 and at the same time kept the boiling point high so that the oxidation was rapid.

The soil is moist when the acid mixture is added, as both soil and chromate are rinsed into the dry flask with 3 ml. of water. Bal (4), Alper (2), and Walkley (14) found that some soils gave low results for nitrogen and carbon unless they were previously moistened with water. There is no indication in this method that any preliminary moistening with water is needed on air-dry soils. If oven-dry soils are used, low results may be obtained unless the soil is allowed to stand in water for some time. Alper attributes the low values in some cases to the formation of complexes which protect part of the carbon from oxidation.

The confining liquid first used in the reservoir was mercury, but this is expensive and it requires the use of an extra trap for KI. Pure glycerine was too viscous to run through the stopcocks with sufficient speed. A 3 to 1 solution of glycerine in water was found satisfactory, and the solubility of the CO_2 is increased very little by the water. In the *International Critical Tables*, vol. 3, page 279, the solubility of CO_2 in pure glycerine is given at 15°C. (partial pressure of CO_2 = 760) as 0 041 cc. per cubic centimeter, whereas a 1.8 to 1 solution of glycerine in water is only 0.046. At 25°C. the solubility is decreased about one fourth.

Thymol blue, with a pH range of 8 2 to 9.4 was used as the indicator. Christensen, Simkins, and Hiatt (6) found that thymol blue was a satisfactory indicator and that acetone added to the absorbing solution sharpened the end point markedly. This is an advantage, as the acetone raises the vapor pressure of the absorbing solution, causing it to boil when the flask is sufficiently evacuated.

The $Ba(OH)_2$ solution must be kept in contact with CO_2-free air and its volume measured accurately, as the excess is titrated and CO_2 determined by difference. The tips of both acid and base burettes are pushed through the stopper so that the solutions drop directly into the flask.

APPLICATION OF THE METHOD

Total carbon

Determinations were carried out on various soils; on pure organic compounds, including those which carbonize on contact with the acid solution (sucrose and thiourea); and on coal. Table 1 gives examples of the results obtained. The agreement with the dry combustion figures is good.

Effect of chlorides

In wet combustion methods, the presence of chloride in the sample causes high results unless special provision is made. The chromyl chloride and chlorine which form during the oxidation will react with the $Ba(OH)_2$ if they reach the absorption flask. To prevent this, Walkley (14) added Ag_2SO_4 in the H_2SO_4 solution, but the value of the Ag_2SO_4 if the chloride content is above 0.2 per cent has been questioned. Others have used $HgSO_4$ or absorption tubes containing KI, $Na_2S_2O_3$, Ag_2SO_4, or $NaHSO_3$.

In the method described here, silver and mercury sulfates or oxides when added to the digestion mixture in various amounts were ineffective in preventing the error if the chloride was 0.25 per cent or more, but KI in an absorption tube was satisfactory. The KI functioned equally well if it was dissolved in the glycerine solution and the reservoir shaken to ensure complete absorption. This eliminated one absorption tube and helped to keep the volume of the apparatus low, reducing the time needed to sweep CO_2 from the train. A sample which contains a considerable amount of chloride when first heated produces red fumes, and a red deposit is formed on the upper part of

the digestion flask. As heating is continued the red deposit disappears and pale green chlorine fumes can be seen to enter the reservoir. Mellor (9, p. 394) cites Thorpe that the chromyl chloride decomposes at 180 to 190° to give chlorine.

TABLE 1

*Determination of total carbon in soils, in pure organic compounds, and in coal by the wet and dry combustion methods**

SUBSTANCE	CARBON	
	Wet combustion	Dry combustion
	per cent	*per cent*
Soils		
P4-1	3.70	3.72
P26-1	2.50	2.52
P28-1	2.28	2.27
P30-1	3.36	3.38
P31-1	1.34	1.33
P50-10	0.79	0.80
P51-1	2.15	2.16
Benzoic acid	68.9	68.8†
Sucrose	42.0	42.1†
Thiourea	15.75	15.80†
Coal‡	74.3	75.5

* Soil samples and dry combustion data supplied by R. W. Simonson, of the department of agronomy, Iowa State College

† Theoretical values.

‡ One-liter absorption flask used. Time, 30 minutes.

TABLE 2

Effect of chlorides on the determination of total carbon in soils

SAMPLE	NaCl ADDED	CARBON FOUND	
		With added NaCl	Without added NaCl
	mgm	*per cent*	*per cent*
1062	0	2.70	2.70
1062	4	2.70	2.70
1062	8.3	2.67	2.70
1062	16.5	2.66	2.70
1062	33.0	2.64	2.70
1062	66.0	2.62	2.70
1062	106.0	2.60	2.70
Benzoic acid	8.3	67.6	68.9
Sucrose	33.0	41.1	42.0

If the chromyl chloride and chlorine are prevented from reaching the absorption flask, the presence of much chloride will cause low results for the carbon. This is a point which has been little stressed but is very clearly shown by the results in table 2. Small amounts of added NaCl did not affect the deter-

mination, but as the chloride was increased, the percentage of carbon decreased. For saline soils containing large amounts of chloride, Walkley suggests the removal of the soluble chloride by preliminary washing with water.

Organic and carbonate carbon

The procedure already described gives the total carbon content of the soil. By a relatively easy change the organic carbon can be determined separately and the carbonate carbon calculated by difference.

The digestion flask is separated from the rest of the apparatus and an air-dry soil sample introduced. Three milliliters of a solution containing 5 per cent H_2SO_4 and 5 per cent $FeSO_4$ is added and the mixture boiled for 1 minute. All the carbonate carbon seems to be removed without loss of organic carbon. The flask and contents are cooled under the tap. Two grams of $K_2Cr_2O_7$ in

TABLE 3

Determination of organic carbon in soils

SOIL NUMBER	PRELIMINARY TREATMENT	ORGANIC CARBON	
		Found after treatment	Known (no preliminary treatment - no carbonate added)
		per cent	*per cent*
1062	5 per cent H_2SO_4	2.69	2.70
1062*	5 per cent H_2SO_4	2.70	2.70
1062*	5 per cent H_2SO_4 + 5 per cent $FeSO_4$	2.70	2.70
1062*	5 per cent H_3PO_4	2.74	2.70
P50-10	5 per cent H_2SO_4	0.490	0.495†

* Twenty-five milligrams of powdered $CaCO_3$ added

† Total carbon minus carbonate by A O.A.C. Calcareous subsoil.

25 ml. of H_2SO_4-H_3PO_4 solution (dissolved by heating and then cooled) is introduced at *B*. The procedure is then carried out as before.

In table 3 the percentage organic carbon from soils with and without added carbonate is shown, after treatment as described above with 5 per cent H_2SO_4 alone, with a mixture of 5 per cent H_2SO_4 and 5 per cent $FeSO_4$, and with 5 per cent H_3PO_4. It will be noticed that the carbonate is not destroyed completely under these conditions by the H_3PO_4 but is removed by the H_2SO_4 and by the H_2SO_4–$FeSO_4$ mixture.

Action of hydrogen peroxide

Degtjareff (8) claimed increased speed of oxidation by the use of hydrogen peroxide with the chromate. Walkley and Black (13), in their examination of the Degtjareff method, point out the action of hydrogen peroxide on the chromic acid and the consequent error if the amount of chromate reduced is used as a measure of the carbon oxidized. They deny, however, the value of

the hydrogen peroxide solution as an aid to the oxidation of the carbon. They believe that water would be equally effective and that either would serve only to generate heat when mixed with the sulfuric acid. In view of these conflicting claims, it seemed worthwhile to examine the problem.

From the results with the apparatus here described, Degtjareff's claim appears to be justified. Three milliliters of 5 per cent H_2O_2 were added to dropping funnel *B* and allowed to enter the reaction mixture at the rate of 1 drop a second after the first vigorous action was over. This allowed the CO_2-free air to be drawn through the apparatus at an increased rate without lowering the CO_2 obtained. It was found that 3 or 4 bubbles a second could be used during the first part of the digestion and 8 to 10 during the second part. With this increased speed the entire procedure has been finished in less than 20 minutes.

A 5 per cent solution of H_2O_2 was more effective than a 1 per cent solution, indicating that it was the peroxide and not the water which increased the speed of the reaction. Also, as the peroxide is introduced when the mixture is already near the boiling point, the effect cannot be a matter of increased heat. It is probably a case of released oxygen from the chromic-acid-peroxide reaction. Adams (1) showed the value of added oxygen in aiding the reaction, but he introduced it as a gas. In methods employing an evacuated flask, the hydrogen peroxide would be preferable.

TABLE 4

Effect of hydrogen peroxide on the determination of carbon in soil 1062

TREATMENT	BUBBLES PER SECOND—SECOND PART DIGESTION	CARBON
		per cent
No H_2O_2	4 to 6	2.70
	6 to 8	2.68
	8 to 10	2.66
3 ml. 5 per cent H_2O_2	8 to 10	2.70
5 ml. 1 per cent H_2O_2	8 to 10	2.67

In table 4 a few results on soil 1062 are shown.

SUMMARY

A wet combustion method is described by which the total carbon in soils and in pure organic compounds can be determined in 20 to 25 minutes with a high degree of accuracy.

Oxidation of the carbon is accomplished by $K_2Cr_2O_7$ in a mixture of H_2SO_4 and H_3PO_4. Speed of oxidation is increased by addition of H_2O_2. The CO_2 set free is measured by collecting it in an evacuated absorption flask containing $Ba(OH)_2$ and by titrating the excess $Ba(OH)_2$ with HCl.

A glycerine solution replaces mercury as the confining liquid for the CO_2.

Potassium iodide dissolved in the glycerine solution prevents the apparent increase in CO_2 when chlorides are present. Results are low, however, if the chloride content is greater than 1 per cent.

Carbonates are removed by boiling in a solution of 5 per cent H_2SO_4 with 5 per cent $FeSO_4$, apparently without loss of organic carbon.

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PHOSPHORUS FIXATION BY SOIL SEPARATES AND FRACTIONS[1]

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When soluble phosphates are added to a soil, a portion combines with the soil. This phenomenon has been generally called "phosphorus fixation." This is an especially fitting term, as pointed out by Murphy (9), because it implies no specific mechanism by which soil removes phosphorus from the soil solution.

The purpose of the present study was to determine those mechanical separates of the soil which are most active in fixing phosphorus, rather than the mechanism of this fixation process itself.

MATERIALS AND METHODS

Soil separates and fractions

Separates of a Wabash soil—a lime-free alluvial soil developed from prairie soils—the surface 6 inches of which are dark colored and contain over 30 per cent clay, were obtained by the sedimentation method of Perkins and King (10). This consists, essentially, in repeatedly working the soil by hand to insure the disintegration of all aggregates, stirring it in a column of water, and syphoning off the supernatant material after a definite period of time. The thoroughness of aggregate disintegration and of the removal of the finer particles was checked by microscopic observation. Pertinent data on the method of separation, as well as information regarding the size of the particles and other soil relationships, are presented in table 1.

A portion of each separate was subdivided into heavy-mineral and light-mineral fractions, as follows: Small amounts of the separate and a solution of bromoform and carbon tetrachloride adjusted to a specific gravity of 2.62 were placed in a tube, and the mixture was well stirred and centrifuged. The material rising to the top was restirred into the bromoform solution without disturbing the bottom precipitate and the mixture was recentrifuged. This process was repeated at least a second time and then the supernatant material was filtered off. Fresh bromoform solution was added to the bottom precipitate, and the mass was stirred and recentrifuged. This process was continued until no more material rose to the top. By this fractionation the heavy minerals (sp. gr. > 2.62) contained the quartz group, and the light minerals (sp.gr. < 2.62), the feldspars, as classified by Jeffries (7).

[1] Contribution No. 263, department of chemistry.

Chemical analyses

The chemical analyses of the Wabash soil, separates, and fractions as reported in table 2, were made by A.O.A.C. methods (1, p. 1–17).

The phosphate in the filtrates described under phosphate fixation was determined by the Denigès coeruleomolybdate method as adapted by Atkins (2).

Phosphate fixation

In the phosphate fixation tests a soil-solution ratio of 1:2½ was used. To 25 gm. of soil in a 500-ml. centrifuge bottle was added sufficient CO_2-free water to make 62.5 ml.; then the designated amount of $Ca(H_2PO_4)_2 \cdot H_2O$ was added from a stock solution. This mixtüre was agitated at 25°C. in a constant temperature room for 18 hours by rotating end-over-end at the rate of 6 r.p.m. The samples were then centrifuged and the supernatant liquid was passed through clay filters. The filters were washed with 0.1 *N* and 0.05 *N* HCl to

TABLE 1

Average measurements of particles in separates of a Wabash soil

SEPARATE	SUSPENSION TIME OF PARTICLES IN 1 FOOT OF WATER	SETTLING TIME OF PARTICLES IN 1 FOOT OF WATER	AVERAGE DIAMETER OF PARTICLES	PER CENT SIZE OF NEXT LARGER GROUP	NUMBER OF PARTICLES PER GRAM	SURFACE PER GRAM OF SEPARATE
			mm		*millions*	*sq cm* *
A		3.33 min.	0.06		3.3	382
B	3.33 min.	20 min.	0.034	56	18.6	670
C	20 min.	2 hr.	0.016	47	177.6	1420
D	2 hr.	12 hr.	0.006	37	3375.0	3815
E	12 hr.	3 days	0.003	50	27000.0	7640
F	3 days		?	?	?	?

* Calculated on assumption that particles were spheres

liberate all absorbed phosphate. The technique for liberating the absorbed phosphate as given by Perkins, King, and Benne (11) was somewhat changed, in that more acid was used to take care of larger amounts of phosphate.

Check analyses on the phosphate adsorbed by the filter were frequently run.

Microscopic measurements

Particle sizes were measured by means of a microscope and an ocular micrometer. One thousand particles were measured for the A and B separates; and 500 for the C, D, E, and F, the particles of which were more nearly uniform. The measurements were averaged, and the results are given in table 1.

There is, of necessity, some overlapping of particle sizes in adjacent groups. Typical measurements show that the smallest particle in A separate was 0.032 mm. in diameter, and the largest particle in B separate, 0.049 mm. It is almost impossible to make an absolutely sharp separation, but the separates were distinct in characteristics. According to the International Society of Soil

Science, the A and B separates would be classified as fine sand; the C, D, and E, as silts; and the F as clay.

RESULTS AND DISCUSSION

As shown in table 2, the proportion of heavy minerals decreased with particle size, until only a trace was found in group E. The scarcity of heavy minerals

TABLE 2

Chemical composition of heavy and light fractions of separates of a Wabash soil

SEPARATE	FRACTION*	PERCENTAGE OF SEPARATE	RATIO LIGHT/HEAVY MINERALS	SiO_2	R_2O_3	Fe_2O_3	$\frac{SiO_2}{R_2O_3}$
				per cent	per cent	per cent	
A	.			90 30	8 72	3 57	.
	A−	53 4	1.15	87.10	9 60	2 14	9.07
	A+	46.6		92.00	7.00	5.30	13.14
B				88 00	7.50?	2.17	
	B−	54 3	1.19	85.70	7 50?	0.98	11.43
	B+	45 7		90.05	10.00	3.34	9.01
C				85.41	11.03	4.06	
	C−	63 7	1.75	84.00	10.06	0 98	8.35
	C+	36.3		88 00	11 65	10 55	7 55
D				70 33	17 58	10.30	
	D−	98 91	90.74	69.39	17 57	10.58	3.95
	D+	1.09		71.42	18 47	17.40	3.87
E				....	.	.	..
	E−	99.99		59.00	30.61	13 02	1.93
	E+	trace		.	. .		. .
F				. .			.
	F−	100 00		46.43	33.03	19.10	1.41
	F+	0.00		...	..		.
Entire soil		...	....	70.37	16.36	8.16	4.30

* Heavy fractions designated by +; light fractions, by −.

in the five groups was checked by chemical analysis and repeated attempts to thoroughly dehydrate and fractionate the D, E, and F fractions.

The separates were salted from suspension by calcium chloride in such a manner that all the particles were saturated with calcium. Perkins and King (10) published data to show that the pH value of calcium soils is about 7. Perkins, King, and Benne (11) have shown that the filtrate from such soils treated with $CaH_4(PO_4)_2$ has a pH value of 5.0 to 5.5. Bradfield, Scarseth, and Steele (5) ascribe phosphate fixation between pH values of 4.5 and 7.0 to

a surface phenomenon, and Benne and his co-workers (3, 4) consider that the calcium ion dominates phosphate fixation at pH values above 5. Several pH determinations on the soil extracts obtained show constant values around 5.25 and entirely within the range of 5.0 and 5.5. Gaarder (6) has shown that with an excess of calcium ions the critical pH value for phosphate precipitation is around 5. The data presented in tables 3 and 4 result from solutions having an excess of calcium.

Curves that might be drawn from the data in tables 1 to 4 would show similar characteristics in the A, B, and C fractions and a sharp break between these

TABLE 3

Phosphate fixation by separates of a Wabash soil

Per cent of added P_2O_5 fixed

SEPARATE	P_2O_5 ADDED, POUNDS PER ACRE						
	200	300	500	1000	2000	5000	10,000
A	98.3	77.1	59.6	.	31.2	16.3	
C	98.2	78.5	62.3	.	27.4	13.7	
D	.	..	97.7	94.7	89.27	66.8	46 5
E	...	.	99.6	..	99.47	97.7	84 6
F	...	.	99.4	..	99.53	98.8	92.8

TABLE 4

Phosphate fixation, on a surface area basis, by separates of a Wabash soil

Mgm. added P_2O_5 fixed per sq. m. surface area

SEPARATE	P_2O_5 ADDED, POUNDS PER ACRE		
	500	2000	5000
A	0.96	2.00	2.63
C	0.27	0.47	0.60
D	0.16	0.67	1.08
E	0.08	0.32	0.78
F	0.04	0.16	0.40

characteristics and those of the D, E, and F fractions. These differences, specifically, are as follows: As time of sedimentation increased uniformly, the particle size decreased somewhat uniformly. All the separates approximated half the diameter of the next larger size except the D separates, which approximated one third the diameter of the C separates. The ratio of light to heavy minerals was between 1 and 2 for the A, B, and C separates but jumped to over 90 for the D, E, and F. The percentages of SiO_2 and R_2O_3 also showed a break between the A, B, and C and the D, E, and F separates. Phosphate fixation showed a decided break here also. At the 500-pound-per-acre application, the A and C separates fixed approximately 60 per cent of the added phosphate but the D, E, and F separates fixed over 97 per cent; at the 2,000-pound application the jump was from below 30 to almost 90 per cent, and at the 5,000-pound level, from about 15 to over 65 per cent.

In most cases phosphate fixation data have not been given for the B separates, as they were erratic and somewhat out of line, and sufficient material was lacking for check analyses.

That the light minerals fix more phosphate than do the heavy minerals is evident from the following fixation percentages at the 500-pound application of P_2O_5: A+, 61.6; A−, 93.3; B+, 77.7; B−, 93.6; C+, 94.7; C−, 95.7. These figures are much greater than those in table 3. The difference seems to be caused by the bromoform treatment of the soils.

Table 4 shows the phosphate fixation, on a surface area basis, at the 500-, 2000-, and 5000-pound-per-acre applications. It is evident from the data that phosphate fixation decreases as particle size decreases, except for the D separate. The break between the C and D separates is clear at the 2000- and 5000-pound additions. The data for the external surface substantiate those of Metzger (8) that surface adsorption plays a small role in phosphate fixation.

SUMMARY

Phosphate fixation was studied in separates and fractions of a Wabash soil ranging from fine sand to clay, which were obtained by sedimentation and bromoform flotation. The results showed that both the chemical composition of the soil minerals and the phosphate fixation were related to particle size. As the particle size decreased, the SiO_2/R_2O_3 ratio decreased and phosphate fixation decreased on a surface area basis but increased on a weight basis. These changes were gradual, until at a diameter of 0.006 mm. there was an abrupt change in the characteristics of the soil particles.

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EVIDENCE IN SUPPORT OF A NEW CONCEPT AS TO THE END PRODUCT OF SUPERPHOSPHATE IN LIMED SOILS[1]

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The concept presented here was developed from findings given in a series of papers that dealt with the P_2O_5 transitions that ensue when superphosphates are mixed with calcic, magnesic, and dolomitic materials outside the soil (6–10, 12, 13, 14, 15–22). One of these materials was a calcium silicate slag of relatively high fluoride content. Admixtures of this slag induced citrate-insolubility far beyond that induced by corresponding admixtures of either high-calcic limestone or the mineral and precipitated calcium silicates (12, 15). The marked diminution in phosphate solubility that developed in the superphosphate-slag mixtures, and also in ammoniated superphosphates, was attributed to the formation of calcium fluorphosphate, a compound analogous to the apatite of rock phosphate, according to the equation:

$$3Ca_3(PO_4)_2 + CaF_2 \rightarrow Ca_{10}F_2(PO_4)_6.$$

The objectives of the present paper are: (*a*) to integrate the findings obtained before and after discovery of the role of fluorides in P_2O_5 retrogradation in limed and in ammoniated superphosphates, and to interpret those findings in terms of soil relationships; (*b*) to ascertain whether the development of fluorphosphate in mixtures of superphosphate and liming materials before incorporation with soils would be registered by a decrease in the uptake of P_2O_5 by plant cultures; (*c*) to acquire pilot information as to whether the fluorides introduced by the silicate slag diminish the effectiveness of subsequent incorporations of superphosphates.

FORERUNNER LABORATORY FINDINGS

The development of citrate-insolubility in the superphosphate-slag mixtures was found to be intensified by high basicity and moisture, by increase in the proportion and the dispersion of fluorides, and in particular, by elevation in temperature. The conclusion as to the cause of the abnormal development of citrate-insoluble P_2O_5 in the superphosphate-slag mixtures was supported by chemical, microscopical, and X-ray examinations of the citrate-insoluble residues. Further substantiation was afforded by (*a*) chemical and microscopical analysis of gently heated moist mixtures of 12 parts of tricalcium

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phosphate and 1 part of pulverulent calcium fluoride, and (*b*) the nondevelopment of citrate-insoluble P_2O_5 when fluoride-free experimental superphosphates were either mixed with fluoride-free liming materials or ammoniated (20). These experimental superphosphates were from phosphoric acid and sulfuric acid acidulations of limestone, defluorinated calcined rock phosphate, and defluorinated fused rock (15, 19, 20, 21).

Beeson and Jacob reported that decrease in P_2O_5 availability occurred in mixtures of ordinary superphosphate and ammonium sulfate with defluorinated calcined rock phosphate (2). Their results were confirmed when commercial superphosphates were used in a duplication of their experimental setup. No diminution of P_2O_5 availability occurred, however, in similar mixtures of fluoride-free experimental superphosphates and defluorinated powdery rock phosphate (19). Likewise, because of limited surface reactions, a glassy, partly defluorinated, fused rock phosphate produced at Wilson Dam was found to be compatible with commercial superphosphates (21).

Sufficiency of component fluorides of superphosphate to induce reversion to calcium fluorphosphate

When the development of a high percentage of calcium fluorphosphate in the superphosphate-slag mixtures first was noted, the phenomenon was considered to have been induced chiefly by the fluoride content of the slag. But even though additive fluorides expedite P_2O_5 reversion when a superphosphate is processed to a basic product, they are not requisite for full retrogradation. The fluorine content of domestic rock phosphate is usually considerably more than the amount called for by the apatite component, and only a small fraction of that fluorine is dispelled by the acidulation process and in the curing of the resultant superphosphate. Hence the quantity of unexpelled fluorides is ample to cause the generated soluble phosphates to undergo complete reversion to the insoluble calcium fluorphosphate when the superphosphate is processed subsequently. The several factors that accelerate this result in limed superphosphates also promote the secondary reactions that induce the formation of tricalcium phosphate (4, 5), and the ultimate formation of calcium fluorphosphate, in unduly ammoniated superphosphates.

Nonreactivity of fluorides toward dibasic phosphates

Calcium fluorphosphate does not develop in mixtures that contain only dicalcium phosphate and calcium fluoride, but it does develop when those mixtures are fortified with basic calcic compounds. The conversion of dicalcium phosphate to tricalcium phosphate was found to be slow and incomplete in mixtures with calcic carbonates and silicates, as well as in aerated aqueous suspensions (7, 8, 10). The conversion of dicalcium phosphate to tricalcium phosphate in mixtures containing an excess of limestone has been found to be less rapid than the successive development of calcium fluorphosphate through reaction between tricalcium phosphate and calcium fluoride.

The magnesium phosphates formed in superphosphate-dolomite mixtures have not been found to react with calcium fluoride, and retrogradation in such mixtures is, therefore, decidedly less than that induced in corresponding mixtures of superphosphate and high-calcic limestone.

INTERPRETATION OF LABORATORY FINDINGS IN TERMS OF P_2O_5 CHANGES THAT OCCUR IN LIMED AND PHOSPHATED SOILS

The present consideration is delimited to incorporations, as distinct from surface applications.

The transitions that occurred in the mixtures of superphosphates and liming materials of the cited studies should occur also when superphosphate additions to the soil are made under the following conditions: (*a*) direct incorporation with previously limed soil; (*b*) incorporation in dry immediate mixtures with multiple proportions of limestone; (*c*) incorporation in moistened mixtures briefly cured with multiple proportions of limestone to an almost complete formation of dicalcium phosphate.

Because of the sluggish nature of the reaction between dicalcium phosphate and calcium carbonate in aqueous suspensions (7) and in wetted mixtures during protracted periods (10), it seems probable that the dicalcium phosphate generated in moderately limed soil will remain in that form for a considerable period. In a soil adequately prelimed, as to rates of and interim between liming and superphosphating, the duration of the generated dicalcium phosphate would be governed by the rate and thoroughness of the superphosphate incorporation. When the superphosphate addition for a given area is incorporated by means of a limestone mixture, obviously the mixture should supply the amount of limestone requisite for the adequate liming of the same area.

Perfect distribution is not to be expected when liming materials and phosphates are incorporated with soils. Hence, when the superphosphate is incorporated simultaneously with an economic addition of limestone, or when the interval between liming and subsequent phosphating is inadequate to effect prior dissolution of the limestone and neutralization of the soil, the water-soluble phosphates suffer fixation by the acidic soil compounds, rather than reaction with the occasional limestone particles. It is apparent also that, although a moderate liming of a superphosphated soil is conducive to the desired formation and persistence of dicalcium phosphate, excessive liming promotes the transition of that phosphate to tricalcium phosphate. But were tricalcium phosphate the end product of superphosphate incorporated with a moderately limed soil, the future availability of the P_2O_5 not removed by the initial crops would not be a serious problem. This is evidenced by the satisfactory response from tricalcium phosphate supplied by ground bone, by defluorinated calcines and fusions of rock phosphate, and by fluoride-free basic slag.

The established role of component fluorides in phosphate retrogradation out-

side the soil points to the probability that superphosphate additions to well-limed soils suffer slow but certain transition to calcium fluorphosphate. Yet even though its composition is that of apatite, an ultimate precipitate of calcium fluorphosphate from superphosphate in a prelimed soil probably would occur as grains of infinitesimal fineness in relation to the particles of pulverized rock phosphate. It would be expected, therefore, that the solubility of calcium fluorphosphate generated within the soil would be far greater than the solubility of incorporated rock phosphate. This solubility relationship has been registered by substantial plant response to the P_2O_5 content of calcium silicate slag after its dissolution and the liberation of its fluorphosphate and silica content within the soil in pot cultures and in the field.

MEASUREMENT OF FLUORIDE-INDUCED REVERSION THROUGH UPTAKE OF P_2O_5 BY RYE SEEDLINGS IN NEUBAUER CULTURES

The distinction between incorporations of granules of calcium fluorphosphate formed in mixtures outside the soil and the dispersed deposition of that compound from a superphosphate incorporation in a prelimed soil was considered in a series of 60 duplicated Neubauer (27) soil cultures. The uptake of P_2O_5 by the rye seedlings of these soil cultures was used to register the effects of calcium fluoride upon the availability of dicalcium and tricalcium phosphates. In one experiment, mixtures of a fluoride-free superphosphate with calcium silicate and with calcium silicate slag (12, 18) were aged 3 months and then incorporated with two soils. The same soils received simultaneous incorporations of tricalcium phosphate, alone and also as a component of its cured mixture with calcium fluoride. In the other experiment, three soils, prelimed and unlimed, received incorporations of calcium fluoride and then were aged before incorporations of dicalcium and tricalcium phosphates. The preadditions of calcium fluoride were made at two rates, to represent the respective amounts of fluorides that would be introduced by slag at rates equivalent to 2 and 4 tons of $CaCO_3$ per 2,000,000 pounds of soil.

Effect of inclusions of calcium fluoride in mixtures of basic calcium phosphates

Two of the four phosphatic treatments of table 1 had been made by mixing a *fluoride-free experimental* superphosphate with fluoride-free calcium silicate and with calcium silicate slag of high fluoride content, in the 1:2 ratio, and aging moist 90 days at room temperature. This moist aging brought no development of citrate-insolubility in the fluoride-free mixtures of superphosphate and calcium silicate, whereas a citrate-insoluble P_2O_5 content of 9.35 per cent had developed in the corresponding mixture that contained the calcium silicate slag of high fluoride content.

Two soils were prelimed with 100-mesh limestone and with 100-mesh slag in respective amounts equivalent to the rate of 3 tons of $CaCO_3$ per 2,000,000 pounds of soil. The limed and the slagged soils and the controls then were aged moist 2 weeks and the phosphatic mixtures that had been aged 90 days

were incorporated. There was a further interval of 2 weeks between phosphating and seeding to rye.

The P_2O_5 uptake from each mixture of the calcium silicate and the fluoride-free superphosphate was considerably greater than that from the corresponding mixture that contained the fluoride-bearing slag. This was true even for the soils that had been prelimed with the 3-ton $CaCO_3$-equivalent of slag, although the P_2O_5 of the slag augmented by 20 per cent the ration supplied by the superphosphate. The mean uptake of P_2O_5 from the six units treated with the mixture of the fluoride-free superphosphate and fluoride-bearing slag was only 51.9 per cent of the mean uptake from the corresponding units fertilized with the fluoride-free mixture of superphosphate and calcium silicate.

TABLE 1

Effect of inclusions of calcium fluoride upon the P_2O_5 uptake from incorporations of basic calcic phosphates by rye seedlings

SOIL	LIMING* TREATMENTS	pH	P_2O_5 UPTAKE†			
			Aged moist mixture of fluoride-free superphosphate		Tricalcium phosphate, moistened and aged	
			With calcium silicate‡	With calcium silicate slag§	Alone‖	With calcium fluoride¶
			mgm	*mgm*	*mgm.*	*mgm*
Hartsells fine sandy loam	None	4.8	8.6	6.2	7.6	4.5
	Limestone	7.0	9.6	4.5	4.5	0.4
	Slag	7.1	10.4	5.3	4.4	1.2
Decatur silt loam	None	6.3	11.0	6.0	5.1	2.8
	Limestone	7.2	12 4	5.0	3.0	1.7
	Slag	7 0	11.9	6.2	6 8	4.6

* The unlimed soils and those limed with 100-mesh materials at the rate of 3 tons of $CaCO_3$ per 2,000,000 pounds of soil were aged moist 2 weeks.

† From the common P_2O_5 incorporations of 25 mgm. per 100 gm of soil, equivalent to the rate of 500 pounds of P_2O_5, soil basis as in *.

‡ This 1:2 mixture was devoid of fluorine and had developed no citrate-insoluble P_2O_5 during aging moist 90 days at room temperature, after which it was incorporated and again aged 2 weeks

§ The mixture and treatment corresponded to those of ‡, but the fluoride content of the slag had induced a citrate-insoluble P_2O_5 content of 9.35 per cent during the 90 days of aging.

‖ Aged alone 6 days at 65°C., the $Ca_3(PO_4)_2$ had a citrate-insoluble P_2O_5 content of 7.82 per cent.

¶ The $Ca_3(PO_4)_2$ + CaF_2 mixture, aged moist 6 days at 65°C., had developed a citrate-insoluble P_2O_5 content of 32.0 per cent.

In the second series of table 1, a laboratory-prepared tricalcium phosphate was incorporated alone and as a component of its aged mixture with precipitated calcium fluoride in the 12:1 weight ratio requisite for the formation of

calcium fluorphosphate. Both the tricalcium phosphate and its fluoride mixture had been maintained moist at 65°C. for 6 days, during which more than 80 per cent of the P_2O_5 content of the mixture had been converted to the citrate-insoluble form. The actual reversion may have been virtually complete, since analytical charges of the generated fluorphosphate are appreciably soluble in the conventional ammonium citrate solvent. This analytical value is reflected by the diminution in the P_2O_5 utilized by the roots and tops of the seedlings. The mean uptake from the six treatments with the 6-day mixture of tricalcium phosphate and calcium fluoride was only 48 per cent of the mean uptake from the corresponding incorporations of unaltered tricalcium phosphate.

In the values registered by tricalcium phosphate, particularly those from the prelimed and the preslagged soils, the P_2O_5 uptake from the straight addition of tricalcium phosphate was less than the uptake from the equivalent P_2O_5 addition as the fluoride-free mixture of superphosphate and calcium silicate. When incorporated, the last-mentioned mixture was composed chiefly of dicalcium phosphate, and the P_2O_5 uptake from this mixture gave no indication that the formation of fluorphosphate had occurred during the growth period, even in the preslagged soil.

Influence of an acquired calcium fluoride content of a soil upon the availability of subsequent incorporations of phosphates

The use of the calcium silicate slag from rock phosphate reduction furnaces as a liming material has reached large proportions in several states. This form of calcium silicate undergoes carbonatation readily in soils, and the disintegration of 2- and 4-ton $CaCO_3$-equivalent incorporations per acre results in respective dispersions of 260 and 520 pounds of calcium fluoride. Concurrent lysimeter experiments indicate that these fluoride increments are not leached readily. It seemed imperative to ascertain whether the fluorides introduced through limings with this slag would exert a repressive effect upon the availability of the P_2O_5 of subsequent additions of superphosphate.

The three prelimed soils of table 2 were aged moist for 2 weeks after incorporation of the respective limestone treatments, none of which had brought the soil to a pH of 7. The aged soils then received incorporations of precipitated calcium fluoride at the 260- and 520-pound rates and were aged 1 week more. Following the two successive preparatory treatments with limestone and calcium fluoride, each fluoride-impregnated soil and its no-fluoride control received an incorporation of dicalcium phosphate, which does not react with calcium fluoride, and an incorporation of tricalcium phosphate which does react with that fluoride. The soil controls that received neither limestone nor fluoride were subjected to the same aging treatment accorded the soils that received limestone and subsequent fluoride additions.

In every case, the P_2O_5 uptake from the dicalcium phosphate of the limed soil was somewhat more than that from the unlimed control. This was true

for the no-fluoride controls, as well as the soils that received the preparatory impregnation of calcium fluoride at the two rates. Since the preaddition of the calcium fluoride caused no decrease in P_2O_5 uptake from any of the 12 units that received subsequent incorporations of dicalcium phosphate, the persistence of that phosphate in the soils is indicated. Apparently, the increase in pH induced by the preliming and the duration of experimental period were not extensive enough to generate tribasic forms in amounts sufficient to repress P_2O_5 uptake. The indication that no appreciable proportion of calcium

TABLE 2

Influence of incorporations of calcium fluoride upon P_2O_5 uptake from subsequent incorporations of dicalcium and tricalcium phosphates

SOIL	LIMESTONE TREATMENT*	pH	P_2O_5 UPTAKE†					
			From dicalcium phosphate			From tricalcium phosphate		
			Without fluoride	With fluoride‡ 13.1 mgm §	With fluoride‡ 26 2 mgm ‖	Without fluoride	With fluoride‡ 13 1 mgm §	With fluoride‡ 26 2 mgm.‖
			mgm.	*mgm*	*mgm.*	*mgm*	*mgm.*	*mgm.*
Montevallo silt loam	none	4.6	9 6	12.0	11.9	7.7	4.5	2.6
	4000	6.4	11.5	12.5	12.3	3.4	3.2	1.6
Hartsells fine sandy	none	4.8	8.4	8.7	8.6	4.0	2.4	2.6
loam	3750	6.3	10.6	10.5	10.9	2.9	1.5	2.3
Fullerton silt loam	none	5.5	11.6	11.6	12.0	7.7	4.2	3.4
	2500	6.4	12.3	13.2	12.9	3.1	1.7	1.9

* Pounds of 100-mesh material, $CaCO_3$ basis, per 2,000,000 pounds of soil. The unlimed soils and those limed were then aged moist 2 weeks.

† From the common incorporation of 25 mgm. of P_2O_5 per 100 gm. of soil; equivalent to the rate of 500 pounds per 2,000,000 pounds of soil.

‡ The incorporations of the precipitated calcium fluoride were made after the 2-week aging of the incorporations of limestone, and the soils were aged 1 week more before the incorporation of the phosphates, after which the soils were wetted four times during a further aging of 2 weeks and then seeded.

§ The amount of fluoride added to the soil before phosphating was equivalent to that carried by the Wilson Dam calcium silicate slag, at the rate of 2 tons of slag per 2,000,000 pounds of soil.

‖ Same as § for the 4-ton rate.

fluorphosphate was formed in these three fluoride-fortified soils during the 31-day period between the incorporation of the dicalcium phosphate and the harvesting of seedlings is in harmony with the laboratory findings that no calcium fluorphosphate develops in either mixtures or highly carbonated water suspensions of dicalcium phosphate and calcium fluoride.

In every instance, the uptake of P_2O_5 from the unlimed and the prelimed controls that received tricalcium phosphate without a preaddition of calcium fluoride was far less than the uptake from the corresponding incorporation of dicalcium phosphate without calcium fluoride. This difference reflects the fact

that, prior to incorporation, one sixth of the P_2O_5 content of the tricalcium phosphate was citrate-insoluble, whereas the dicalcium phosphate was 100 per cent citrate-soluble.

Without exception, the prior impregnation of calcium fluoride caused a diminution in uptake of P_2O_5 from the subsequent incorporations of tricalcium phosphate with unlimed and with prelimed soils. This indicates that the 31-day interval, accounted for jointly by the 14-day preliminary phosphate-aging period and the 17 days of seedling growth, was long enough to induce a considerable development of calcium fluorphosphate when the incorporated phosphate was in the form susceptible of immediate reaction with the calcium fluoride previously incorporated.

The indications from the two Neubauer culture experiments are in harmony with the laboratory findings as to (*a*) the slow formation of tricalcium phosphate from dicalcium phosphate in its mixtures with either limestone or calcium silicate, and (*b*) the absence of any fluoride effect upon P_2O_5 solubility in mixtures of superphosphate and limestone, so long as the generated dicalcic phosphate continues as such. The culture studies likewise support the laboratory findings as to the marked influence exerted ultimately by component calcium fluoride upon the availability of the tricalcium phosphate generated in ammoniated superphosphates.

INTERPRETATION IN TERMS OF SOIL RELATIONSHIPS

In moist mixtures, monocalcium phosphate and two hydrogen equivalents of pulverized limestone react to form dicalcium phosphate, speedily and almost completely, at ordinary temperatures. It is obvious that the dicalcium form is the only phosphate generated in such mixtures. In corresponding mixtures containing more than two hydrogen equivalents of limestone, the succeeding reaction between the two solids, dicalcium phosphate and limestone, is sluggish and protracted. There is no reason to assume that similar relationships do not obtain in a prelimed and subsequently phosphated soil.

Since the transition of dicalcium to tricalcium phosphate is slow and requires an excess of reactant calcic compounds, it seems probable that a well-mixed incorporation of superphosphate in a soil effectively prelimed would result in a protracted occurrence of dicalcium phosphate. The ideal would be to effect complete neutralization of the acidic and phosphate-fixation properties of the soil by a thoroughly disseminated liming material during an adequate interval before incorporation of the acidic superphosphate. This ideal is not attained by economic incorporations, and localized acidic soil zones and particles of undecomposed limestone are to be expected in practice.

It would seem even more likely that the direct incorporation of dicalcium phosphate as a component of a superphosphate-limestone mixture would assure the prolonged occurrence of that phosphate in a prelimed soil. The dicalcium phosphate would continue as such, most probably, even in an acidic soil when a simultaneous liming and dicalcium phosphate treatment is provided by the

incorporation of a briefly cured mixture of superphosphate and multiple proportions of wetted limestone.

In a soil inadequately limed, that fraction of an incorporation of water-soluble P_2O_5 that does not undergo fixation by the unaltered soil complexes will be converted to dicalcium phosphate quickly, with a slow progression to tricalcium phosphate. In a soil limed to neutrality, and more especially to basicity, a larger proportion of soluble P_2O_5 will be converted to tricalcium phosphate, which has been assumed to be the ultimate calcium phosphate resultant from a superphosphate addition to limed soils. But, because of the concomitant introduction of reactant component fluorides, tricalcium phosphate is not the ultimate basic phosphate generated from superphosphate in a limed soil.

It has been shown that incorporated fluorides are retained by soils limed with high-calcic limestone (11) and that development of calcium fluorphosphate is accelerated by high pH. The conditions and components essential to the ultimate formation of calcium fluorphosphate prevail, therefore, in a well-limed and superphosphated soil. Hence, both the partial "recovery" of P_2O_5 from superphosphate additions to a moderately limed soil and the repressive effect of heavy liming upon response from superphosphate can be explained, in part at least, by the concept that some of the added water-soluble phosphate is converted ultimately to calcium fluorphosphate.

The final reaction in this ultimate transition, or generation of precipitated apatite from additions of superphosphate, in prelimed soil corresponds to the geochemical phenomenon whereby the apatite of raw rock phosphate was formed by reaction between tricalcium phosphate and infiltrated solute fluorides. Clark (3) discussed the probability that this postulated geological transition accounts for the formation of rock phosphate whereby phosphatic deposits have been preserved for posterity. The theme was elaborated recently by Mansfield (24) in a treatise on the possible relationship between a period of volcanic emissions of fluorine gases and the age of a specific geological formation of apatite. Moreover, the marked affinity of tricalcium phosphate for calcium fluoride has been demonstrated and implemented by utilizing either added or generated suspensions of tricalcium phosphate to form a fluorphosphate floc that removes fluorides from natural waters (1, 16). The same beneficial result has been achieved by means of activated bone filters, as the culmination of extended investigations at the Arizona Agricultural Experiment Station (26).

PRACTICAL CONSIDERATIONS

The P_2O_5 content of the rye seedlings indicates that calcium fluoride exerts no detrimental effect upon the availability of dicalcium phosphate in the soil but does decrease the availability of tricalcium phosphate. The conditions that favor persistence of dicalcium phosphate are the ones that should give the best returns from superphosphate additions to limed soils. Either inade-

quate rates or poor distribution of liming materials will allow subsequent additions of soluble phosphates to be fixed by the acidoids of unneutralized soil zones, whereas excessive liming induces accelerated progressions to tricalcium phosphate and calcium fluorphosphate. The present findings do not demonstrate, however, that the ideal behavior of the superphosphate incorporated in a prelimed soil can be prolonged beyond the first crop.

It has been demonstrated that a fluoride-free superphosphate suffers no serious P_2O_5 retrogradation in its mixtures with liming materials or upon ammoniation. The advantages of that type of superphosphate are obvious. It would not introduce reactant fluorides in the soil and it could be used advantageously in hydroponics and as a cattle feed supplement in limestone mixtures. A low fluoride content also eliminates the danger of the fluoride-induced toxic effect that concentrated superphosphate may exert upon seed germination (25). Moreover, fluoride-free superphosphates could be ammoniated far beyond the extent now feasible in the art without P_2O_5 retrogradation. This would be of economic advantage in the manufacture of commercial fertilizers. A concentrated superphosphate of greatly diminished fluoride content can be made (23), and its production represents a challenge to the industry.

SUMMARY

Phosphate-transition findings obtained before and after discovery of the role of fluorides in P_2O_5 retrogradation in limed and in ammoniated superphosphates have been interpreted in terms of soil relationships.

Because of the sluggishness with which the dicalcium phosphate generated in superphosphate-limestone mixtures and suspensions is converted to tricalcium phosphate, the nondevelopment of citrate-insoluble phosphates therein during the persistence of the dicalcic compound, the ultimate development of calcium fluorphosphate through reaction of the generated tricalcium with component fluorides, and other related factors, it is concluded that the most effective utilization of *incorporations* of superphosphate is to be expected from conditions conducive to a prolonged occurrence of dicalcium phosphate in the soil. The advantage of an adequate lapse between liming and superphosphate incorporation is pointed out.

The uptake of P_2O_5 by rye seedlings indicated that the ultimate calcium fluorphosphate formed as granules in mixtures of superphosphate and limestone outside the soil was less "available" than that formed as dispersions from incorporations of superphosphate within prelimed soils.

Since readily decomposable quenched calcium silicate slag is being used extensively as a liming material, calcium fluoride incorporations corresponding to those introduced by 2- and 4-ton $CaCO_3$-equivalences of slag per acre were made to prelimed soils and aged prior to subsequent phosphatic treatment and seeding. These increments of fluorides exerted no repressive effect upon the uptake of P_2O_5 supplied as dicalcium phosphate, but they repressed sub-

stantially the uptake from corresponding incorporations of tricalcium phosphate.

It is concluded that any fraction of a superphosphate incorporation not "fixed" and not used by the plant in a prelimed soil will suffer ultimate reversion to the fluorphosphate, $Ca_{10}F_2(PO_4)_6$, that characterizes raw rock. Although the formation of this ultimate phosphatic compound in mixtures outside the soil has been demonstrated and indicated by plant cultures as occurrent within limed and phosphated soils, the extent to which the phenomenon may become of practical importance is to be established.

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AIR AND SOIL TEMPERATURES IN A CALIFORNIA DATE GARDEN[1]

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The importance of climate in the growth and fruit production of the date palm, *Phoenix dactylifera* L., has been recognized for many years. Principal emphasis has been upon the temperature of the air and the amount of precipitation during the season of fruit harvest, however, and very little study has been made of the soil temperatures in date gardens. Vinson (7) published curves representing the daily temperatures at 7 a.m. of soil 1 foot below the surface at the Cooperative Date Orchard, Tempe, Arizona, for 1906 and 1907. In 1918, Mason (4) recorded temperatures of soil at the United States Date Garden, Indio, California, at a depth of 2 feet.

The data in this paper were obtained between September, 1934, and January, 1939, in connection with pathological studies on the Omphalia root rot of date palms. Since these temperature readings provide information of wider application than that for which they were originally intended, they are presented separately here. This paper contributes principally to knowledge of the environment of date roots, but it contains certain observations and describes certain methods which may be of interest to the soil physicist.

TEMPERATURE READINGS

A two-roomed, standard instrument shelter was set up halfway between two rows of mature Deglet Noor date palms in block II of the United States Date Garden at Indio, California, at the intersection of the diagonal lines of a 30-foot tree square. The soil at this location is in a transition zone between Indio very fine sandy loam and Indio loam. Samples of soil taken at the site of the instruments indicated fine sandy loam to a depth of 2 feet, fine sand with a small amount of clay in the third foot, and fine sand of uniform color and texture at a depth of about 3 to 8 feet.

The vertical distribution of roots[3] of a near-by date palm was ascertained (table 1) by weighing the roots from a trench which extended 14 feet from the

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trunk. The trench was 2 feet wide and 8 feet deep. More than 97 per cent of the roots (by weight) were found in soil between 1 and 6 feet in depth.

The surface of the soil was kept free from weeds and cover crop during the period of the temperature readings. Overhanging leaves of the surrounding date palms afforded partial shade for the instrument shelter and for the soil in which the soil thermometers were buried. The soil about the instruments was irrigated and cultivated in much the same manner as that in other parts of the date garden.

A thermograph and maximum-minimum thermometers were installed in the upper room of the shelter, and in the lower room was placed the instrument head of a dual soil thermograph. The grid-type bulbs of this thermograph were buried in a horizontal position on the south side of the shelter at depths of 1 and 3 feet, respectively. These bulbs were placed against a wall of undisturbed soil, but the soil to the south of them was disturbed when the

TABLE 1

Vertical distribution of roots of date palm in soil near the temperature instruments

DEPTH	WEIGHT OF ROOTS
feet	*per cent*
0–1	1.7
1–2	15.4
2–3	26.4
3–4	23.6
4–5	24.7
5–6	7.2
6–7	0.3
7–8	0.7

instrument was installed and again in September, 1937, when it had to be repaired.

Weekly mean temperatures of the air and of the soil (table 2) at 1- and 3-foot depths were calculated from the thermograph charts by means of a planimeter. Modifications of this method had been used previously by Shaw (5) and by Cressman et al. (1). To determine the mean temperature, a portion of the curve was selected which represented seven or, less accurately, six consecutive units of 24 hours each. Perpendicular lines were dropped from the ends of this portion of the curve to a base line which was chosen to coincide with any one of the horizontal lines on the graph that did not intersect the temperature curve. Thus, an irregularly shaped figure was formed, bounded above by the temperature curve, on the sides by the vertical lines, and below by the horizontal base line. The area of this irregular figure was then measured by means of the planimeter. This value was divided by the length of the horizontal base line to determine the altitude of a rectangle of equal area and of equal base. The altitude of this rectangle was constructed as a line per-

TABLE 2

Weekly mean temperatures of air and soil, United States Date Garden, Indio, California, September, 1934, to January, 1939*

DATE, WEEK ENDING:	TEMPERATURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS						DATE, WEEK ENDING:	TEMPERATURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS					
		1 foot	3 feet	4 feet	6 feet	7½ feet	8 feet			1 foot	3 feet	4 feet	6 feet	7½ feet	8 feet
	°F.	°F.	°F.	°F.	°F.	°F.	°F.		°F.	°F.	°F.	°F.	°F.	°F.	°F.
1934															
Sept. 3	90	83	81					Nov. 5	70	66	69	70			
10	90	85	81					13	70	67	69	68			
17	83	77	79					19	66	67	69	69			
24	84	79	78	77				26	58	61	67	68			
Oct. 1	72	72	76	75				Dec. 4	50	54	54	64			
8	81	70	74	73				10	57	52	61	63			
15	76	73	73					17	59	57	61	63			
23	66	69	72	72				25	53	55	61	.			
30	71	65	70	70				31	51	53	59				
1935															
Jan. 7	50	53	59	61				July 1	86		77	78	73	71	
14	51	53	58					8	84	76	77	76	74	72	
22	45	50	57	59				15	94	84	78	78	74	72	
28	54	52	57	.				22	92	85	80	78	75	74	
								29	95	88	82	80	76	73	
Feb. 5	64	55	57	60											
11	53	55	58					Aug. 6	92	85	82	80	76	74	
18	55	53	57	60				13	94	88	82	81	77	74	
26	61	56	59					19	85	81	81	80	77	75	
								26	90	83	81	80	77	75	
Mar. 5	56	55	58	60	63										
11	53	53	58	60	63			Sept. 2	90	82	81	80	77	76	
19	63	52	56	59	62			10	89	82	81	79	77	76	
26	58	56	58	60	63			16	91	78	79	78	77	76	
								23	85	81	79	78	77	76	
Apr. 1	68	59	58	62	63			30	81	76	78	77	76	75	
9	68	60	61	62	64										
16	69	63	61	64	64			Oct. 8	77	77	77	76	76	75	
23	74	67	64	66	66			15	72	72	76	74	75	75	
30	71	65	65	66	66			21	68	69	73	73	74	74	
								29	65	67	71	71	73	74	
May 8	69	65	65	66	66										
14	71	67	66	67	66			Nov. 4	59	64	70	70	73	74	
20	75	67	66	68	67			12	52	56	65	66	71	72	
27	83	69	68	69	68			19	49	55	62	64	70	71	
								26	56	56	61	63	68	70	
June 4	83	74	69	71	69										
10	91	77	73	73	70			Dec. 3	57	59	61	63	67	70	
17	88	79	75	75	71			9	55	57	62	63	67	69	
24	88	..	75	76	72	70		17	52	53	60	61	66	68	
								23	51	52	57	60	65	68	
								31	48	51	56	60	64	66	

* Temperatures of the air and of the soil at 1- and 3-foot depths were recorded continuously by thermographs, and weekly mean temperatures were calculated from the thermograph charts by means of a planimeter (see text description of method used). Temperatures of soil at depths of 4, 6, 7½, and 8 feet were determined by weekly readings on standard thermometers.

TABLE 2—*Continued*

DATE, WEEK ENDING:	TEMPERATURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS						DATE, WEEK ENDING:	TEMPERATURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS					
		1 foot	3 feet	4 feet	6 feet	7½ feet	8 feet			1 foot	3 feet	4 feet	6 feet	7½ feet	8 feet
	°*F.*	°*F.*	°*F.*	°*F.*	°*F.*	°*F.*	°*F.*		°*F.*	°*F.*	°*F.*	°*F.*	°*F.*	°*F.*	°*F.*
1936															
Jan. 6	51	51	56	58	64	66		July 6	93	82	82	78	74	72	
13	52	53	56	58	63	66		13	86	82	83	78	75	73	
20	51	51	56	58	62	65		22	96	83	83	78	76	74	
28	53	51	56	57	62	65		28	90	88	85	81	76	74	
Feb. 4	54	53	56	58	62	64		Aug. 3	91	84		80	78	75	
10	52	54	57	58	62	64		10	92	84		80	77	75	
17	59	57	57	59	62	64		18	93	84		80	78	76	
24	58	57	59	59	62	64		24	88	81		80	78	76	
Mar. 2	64	57	59	60	62	64		Sept. 1	91	83					
10	71	64	61	62	63	64		8	80	77		78	77	76	
16	70	66	64	64	64	64		15	83	77		78	77	76	
23	70	65	65	64	64	65		21	83	75		76	76	76	
30	59	60	64	63	64	65		29	82	77		76	76	76	
Apr. 6	61	58	63	62	64	65		Oct. 6	74	71		74	75	75	
13	75	64	63	63	64	65		12	76	71		74	75		
20	80	69	67	66	65	65		20	72	71		73	74		
27	79	72	69	68	66	66		28	69	67		71	73		
May 4	77	71	70	69	67	67		Nov 3	66	66		70	72		
11	82	73	71	70	68	67		10	58	60		69	71		
19	87	78	74	73	69	68		17	62	60		66	70		
25	83	77	75	73	70	69		24	68	62		66	69		
June 1	74	76	75	73	71	70		Dec. 1	56	60		65	68		
8	76	72	74	72	71	70		7	50	55		63	68		
15	90	78	75	74	71	70		14	52	54		61	66		
22	93	81	78	76	72	71		21	56	54		60	65		
29	93	84	80	76	73	71		28	53	55		60	65		
1937															
Jan. 5	46	51		59	64			Apr. 7	68	58		59	60	62	
13	41	47		56	63	66		14	74	61		61	61	62	
19	44	43		55	62	65		21	77	65		62	62	62	
25	34	42		54	61	64		28	70	63		64	63	63	
Feb. 2	47	43		53	59	63		May 5	78	64		64	64	64	
10	53	49		54	59	62		11	74	66		66	64	64	
17	57	49		56	59	62		18	90	73		68	66	66	
25	58	53		56	59	62		25	79	72		70	68	66	
Mar. 3	59	52		56	59	61		June 1	72	72		70	68	68	
11	67	56		57	59	61		8	82	74		71	69	68	
18	62	57		58	60	62		15	80	75		73	70	69	69
24	56	55		58	60	62		22	86	76		74	71	70	70
31	61	55		58	60	62		29	94	81	78	76	72	70	70

TABLE 2—*Concluded*

Date, week ending:	Temperature of air	Temperature of soil at different depths						Date, week ending:	Temperature of air	Temperature of soil at different depths					
		1 foot	3 feet	4 feet	6 feet	7½ feet	8 feet			1 foot	3 feet	4 feet	6 feet	7½ feet	8 feet
	°F.	°F.	°F.	°F	°F.	°F.	°F.		°F.	°F.	°F.	°F.	°F.	°F	°F.
1937—Continued															
July 6	98	83	79	77	73	72	72	Oct. 5	78	74	77	78	77	77	77
13	91	85	81	79	75	72		12	77	72	75	76	76	76	76
21	92	82	80	78	76	74	73	19	77	71	74	75	75	75	75
26	97	84	82	79	76	74	74	26	79	72	73	74	74	75	..
Aug. 3	91	83	81	80	77	75	74	Nov. 2	75	70	73	74	74	75	75
10	92	84	82	80	77	76	75	9	70	69	72	72	73	74	74
16	96	85	82	80	78	76	75	16	64	64	69	70	72	73	73
24	94	85	82	81	78	76	76	23	64	64	68	69	71	72	73
31	93	83	81	80	78	77	76	30	63	64	67	69	70	72	72
Sept. 7	90	80	80	80	78	77	77	Dec. 8	62	62	66	68	70	71	72
14	93	85	81	80	78	77	77	13	62	61	65	66	69	71	71
21	92	80	81	80	78	77	77	20	60	58	63	65	68	70	71
28	83	79	79	79	78	77	77	27	54	54	60	64	67	69	70
1938															
Jan. 4	58	56	60	63	66	68	69	July 5	83	78	75	75	73	72	71
10	57	56	59	62	65	67	69	12	82	81	75	76	73	72	72
20	57	57	60	62	65	67	68	20	94	85	78	76	74	73	73
24	59			62	64	67	68	26	90	85	79	79	76	74	73
31	57	54	59	61	64	66	67								
								Aug. 3	92	86	80	80	77	75	75
Feb. 8	55	53	57	60	63	65	66	8	89	84	80	80	77	75	75
14	56	54	57	60	63	65	66	16	89	83	80	80	78	76	75
21	56	55	58	60	63	64	65	23	86	79	78	78	77	76	75
								30	89	80	78	78	77	76	76
Mar. 2	61	57	58	62	63	64	65								
8	57	56	58	61	63	65	65	Sept 6	90	82	79	79	77	76	76
14	60	57	59	61	63	64	65	12	84	79	78	78	77	76	76
23	64	58	59	62	63	64	65	21	84	78	77	78	77	76	76
29	61	59	61		63	64	65	27	87	79	77	78	76	76	76
Apr. 4	61	57	60	61	63	64	65	Oct. 4†							
12	68	60	60	63	63	64	65	11	83	78	78	74	75	76	75
20	70	61	61	63	64	64	65	17	72	68	70	74	74	75	75
25	75	64	62	66	64	65	66	26	72	68	70	71	73	74	74
								31	72	71	70	73	73	73	74
May 4	67	62	63	64	64	65	66								
9	74	62	62	65	65	65	66	Nov. 7	62	69	70	72	73	73	73
17	81	70	66	68	68	66	66	15	54	62	67	68	72	72	72
24	73	68	67	69	67	67	67	23	58	55	62	65	69	71	71
31	76	78	70	72	68	68	69	30	53	54	60	64	63	70	71
June 8	90	79	73	73	70	69	69	Dec. 7	62	55	60	64	67	70	70
13	76	76	72	73	71	70	70	14†							.
21	84	80	74	74	73	70	70	20	61	60	61	63	67	68	68
28	90	78	75	74	73	71	71	28	49	53	59	62	66	67	68
1939															
Jan. 3	52	51	57	61	65	67	68								

† Records misplaced.

pendicular to the horizontal base line. The point at the upper end of the perpendicular was taken as a temperature reading representing the mean weekly temperature on the graph.

For the measurement of soil temperatures at depths of 4, 6, 7½, and 8 feet, standard thermometers encased in metal armor were lowered by means of copper wires in galvanized iron pipes. These pipes had been inserted in vertical holes made by driving a soil tube into the soil to the different desired depths. The bulbs of the thermometers, except the lower end which touched the soil, were covered with adhesive tape to prevent undercooling by the evaporation of moisture when the thermometers were raised to the surface for reading. The exposed ends of the pipes were kept tightly closed with rubber stoppers to which the copper wires were attached. Readings were made on these standard thermometers once each week (table 2) at the time when the thermograph charts were changed.

The accuracy of the air thermograph was checked by comparison with the maximum and minimum air thermometers. There was no direct method of checking the accuracy of the soil thermograph until June, 1937, when standard thermometers were also placed at depths of 1 and 3 feet. The mean weekly temperatures, however, had been plotted on a large graph from the beginning of the experiment, and it was possible to detect any large inconsistencies in the records by inspecting this graph. The standard thermometers were compared from time to time with a certified thermometer which was thought to be very accurate.

DISCUSSION

Because of limited space, it is not possible to show all the data graphically. Certain parts of the temperature curves are reproduced, however, to illustrate points of special interest. One of the outstanding features of these records is the wide seasonal variation shown in the air temperature. In 1937, the mean weekly air temperatures (fig. 1) varied from 34°F., in January, to 98°, in July; the minimum air temperature for the year was 14°, and the maximum, 114°. During all the years in which records were taken, the mean weekly temperatures of the air were considerably higher in summer than those of the soil at the 1-foot depth. In winter the mean weekly temperatures of the air were usually as low as those of the soil at the 1-foot depth or were somewhat lower.

These findings agree in general with those of Harrington (2) in Saskatchewan. But in southern Ontario, Kimball, Ruhnke, and Glover (3) found the average monthly temperatures of the air to be lower than those of the soil at a depth of 1 foot, with the exception of one month (May, 1931), when the air and soil temperatures were alike. At Davis, California, Smith (6) found that from April 3 to September 30, 1925, the weekly average temperatures of the air were always below those of the soil at a depth of 1 foot and that, except for three weeks, they were also below the weekly average temperatures of soil at a depth of 3 feet. A similar condition was found by Smith (6) between January 8 and July 18, 1927.

The differences between our data and those noted in the reports of these observers, especially the differences between our data for southern California and Smith's data for northern California, are not easily explained. Differences in data from different localities do exist, however, as shown by later observations in an orange orchard near Anaheim, California.[4] It was found that in summer the weekly mean temperatures of the air seldom exceeded those of the soil at a depth of 3 feet and that they rarely approached the weekly mean temperatures of the soil at a depth of 1 foot. Indio is 80 miles inland in an arid valley between two ranges of mountains, whereas Anaheim is on the

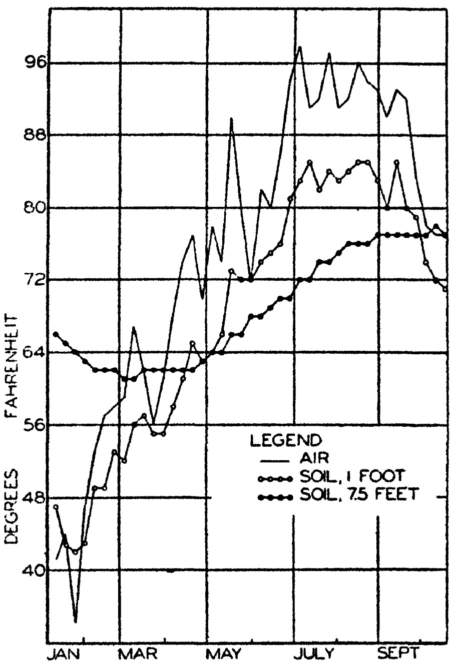

FIG. 1

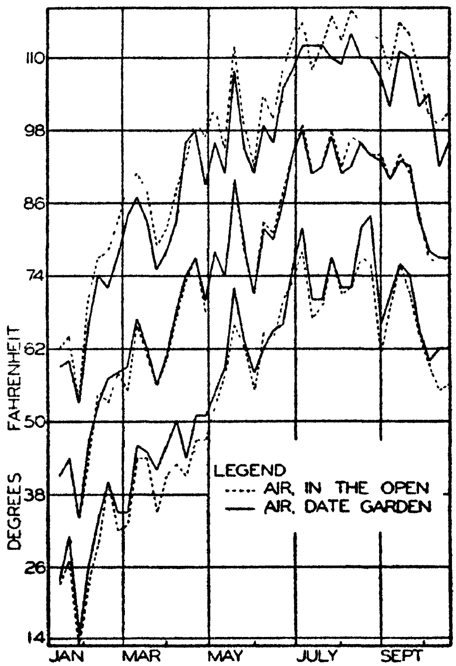

FIG. 2

FIG. 1. VARIATIONS IN MEAN WEEKLY TEMPERATURES OF AIR AND SOIL, 1937

FIG. 2. ABSOLUTE WEEKLY MAXIMUM AND MINIMUM TEMPERATURES AND MEAN WEEKLY TEMPERATURES OF AIR IN THE DATE GARDEN AND IN THE OPEN, 1937

flood plain of the Santa Ana River, only 12 miles from the coast. Although the climate at Indio is typical of that in the Colorado Desert and the climate at Anaheim is similar to that along the Pacific Coast, the basic reasons for the observed differences in relative air and soil temperatures are not well known and must await further investigation.

After the freezing temperatures of January, 1937, it was noted that the grapefruit trees near Indio had been severely injured. Trees that were inter-

[4] Unpublished data on file at the University of California Citrus Experiment Station, Riverside, California.

planted between tall date palms were, as a rule, less affected than those standing alone or in regular orchard formation. Since our air thermograph was situated beneath the overhanging leaves of tall date palms, the recorded temperatures were thought to resemble those about the interplanted grapefruit trees. The meteorological station of the United States Date Garden, on the other hand, was so situated, in the open about 100 yards to the west, that the thermograph there recorded temperatures considered similar to those about the grapefruit trees in the open. When the absolute maximum and minimum air temperatures at the two stations were compared (fig. 2), it was found that the date palms had exerted a tempering effect on the air tempera-

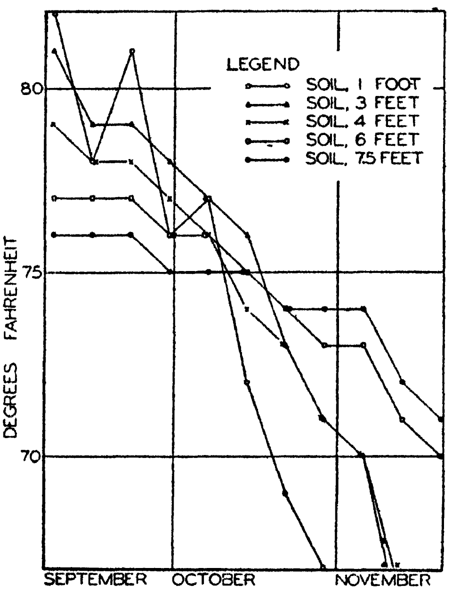

FIG. 3

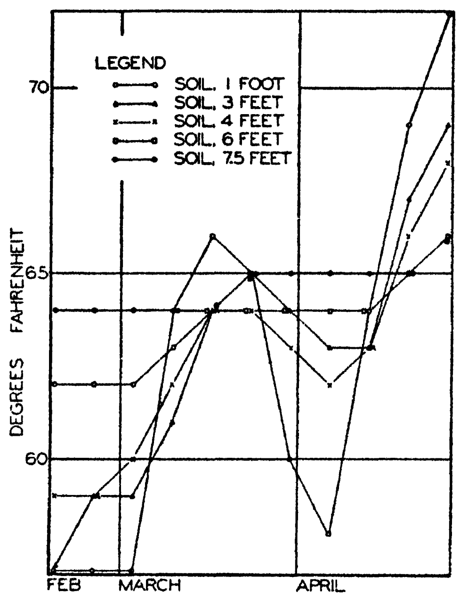

FIG. 4

FIG. 3. OVERTURN OF MEAN WEEKLY SOIL TEMPERATURES, OCTOBER, 1935
FIG. 4. OVERTURN OF MEAN WEEKLY SOIL TEMPERATURES, MARCH AND APRIL, 1936

tures within the date garden. During most of the 7-day periods throughout the year, our thermograph under the palms registered higher minimum temperatures and lower maximum temperatures than did the thermograph in the open. The mean weekly air temperatures at the two stations were nearly identical, however.

Overturns[5] in the temperature of the soil at different depths occurred regularly in the fall and in the spring of each year. As a rule, the overturn in the fall (fig. 3) occurred during September and October. The transition from

[5] The term "overturn" is used in this paper to denote the period of time during which the mean weekly temperatures of soil at different depths were undergoing a complete reversal in relative value.

summer to winter was characterized by relatively gradual changes in temperature. In spring, however, the overturns (fig. 4) were less regular, because of intermittent periods of heat and cold. Beginning in March or April, the spring overturns lasted from 48 to 111 days and were not completed until May or June, whereas the fall overturns (exclusive of 1934) ranged in length from only 35 to 49 days.

The yearly range of air temperatures was considerably greater than that of soil at a depth of 1 foot. As shown in other studies of this kind, the yearly range of soil temperatures diminished with increasing depth of soil (table 3). There was marked evidence of lag in the time at which the soil at different depths reached the yearly maximum and minimum temperatures. When compared with the air-temperature curve (fig. 1), the temperature curve for soil at the 1-foot depth showed a brief lag, and that for the soil at the 7½-foot depth lagged for several weeks. The soil thermograph records for 1- and 3-foot depths showed slight diurnal fluctuations and also marked seasonal fluctuations. It is probable that the fluctuations which affected the thermometers at depths of 4 to 8 feet were entirely seasonal in character.

TABLE 3

Yearly range of air and soil temperatures, United States Date Garden, Indio, California, 1935 to 1938, inclusive

YEAR	TEMPERATURE OF AIR	TEMPERATURE OF SOIL AT DIFFERENT DEPTHS					
		1 foot	3 feet	4 feet	6 feet	7½ feet	8 feet
	°F.	°F.	°F.	°F	°F.	°F.	°F.
1935	28–112	47–92	55–84				
1936	32–114	48–90	54–87	57–81	62–78	64–76	
1937	14–114	40–88	—82	53–81	59–78	61–77	—77
1938	34–114	51–89	55–82	60–80	63–78	64–76	65–76

SUMMARY

Data on the weekly mean temperatures of air and soil within the United States Date Garden at Indio, California, from September, 1934, to January, 1939, are presented. The temperatures of the air and those of the soil at 1- and 3-foot depths were recorded continuously by thermographs, and weekly mean temperatures were calculated from the thermograph charts by means of a planimeter. Temperatures of soil at depths of 4, 6, 7½, and 8 feet were determined weekly on standard thermometers.

Wide seasonal variations in weekly mean air temperatures were found. During the summer months the temperatures of the air were considerably higher than those of the soil at a depth of 1 foot. The large date palms which surrounded the instruments had a tempering effect on the air temperatures within the date garden, but the mean weekly air temperatures were almost identical with those at a near-by meteorological station located in the open.

Overturns in the temperature of the soil at different depths occurred regularly in the fall and spring of each year.

The yearly range of air temperatures was considerably greater than that of soil at a depth of 1 foot; the yearly range of soil temperatures diminished with increasing depth of soil.

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INFLUENCE OF ORCHARD SOIL MANAGEMENT UPON THE INFILTRATION OF WATER AND SOME RELATED PHYSICAL CHARACTERISTICS OF THE SOIL[1]

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Pennsylvania Agricultural Experiment Station

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One of the problems confronting modern agriculture is to devise methods by which man can obtain his food and clothing from the soil without bringing about undue destruction of this most important natural resource. All of our production practices must be continually examined in order to determine to what degree the "two blades of grass" which we seek to produce may be obtained without exposing the soil to some form of destruction. One characteristic of the soil, the vulnerability of which was formerly underestimated but which is now receiving greater attention, is the physical condition, which is controlled and determined by many management practices and which itself controls many physiological responses of plants.

The investigation reported in this paper was conducted in an experimental orchard at the Pennsylvania State College. This orchard was laid out in 1927 to determine the relative value and effects of different cover treatments upon factors determining the yield and welfare of the trees. The orchard, which has a rather gentle and uniform slope of 3 to 8 per cent is divided into six plots, each two rows wide and running up and down the slope. The plots chosen for this study were as follows: plot 1, cultivated annually with a cover crop of rye seeded in the fall and millet seeded in the spring; plot 2, in permanent alfalfa sod; and plot 4, in permanent bluegrass sod.

Every spring the sod plots are torn up with a spring tooth harrow. By midsummer the sods have usually reestablished themselves. Phosphorus and potassium applications were alike on all plots studied. Plot 4 receives annually 10 pounds of nitrate of soda per 40 foot square. Plots 1 and 2 received no nitrogen.

For comparison with the orchard plots, studies were made also upon an alfalfa hay field (plot 3) and a woodlot (plot 5) both adjacent to the orchard.

In 1935, in cooperation with the Soil Conservation Service, the space between two rows in each orchard plot was banked with a ridge of soil to confine its

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runoff to its own area and a tank was constructed at the foot of the slope to catch the soil and water removed by erosion. The runoff and erosion data supplement the data obtained in this study in showing both the cause and the effect of the physical changes brought about in the soil.

The general purpose of this investigation was to determine what effect these different cover practices have had upon the physical condition of the soil and its moisture status, particularly with reference to infiltration, which is important as a means not only of decreasing erosion but also of storing in the entire soil mantle sufficient moisture to bridge over the drought periods.

EXPERIMENTAL

The studies herein presented consisted of the correlation between certain physical conditions produced within the soils as a result of cover treatment and the moisture status of the soil as measured by infiltration and runoff.

TABLE 1

Volume weights of the surface soil, by 3-inch layers in experimental plots

(Average of 10 samples)

PLOT	TREATMENT	1ST 3-INCH LAYER		2ND 3-INCH LAYER	
		Volume weight	Standard error	Volume weight	Standard error
1	Cultivated and cover-cropped orchard	1.55	±0.02	1.54	±0.03
2	Alfalfa sod orchard	1.42	±0.02	1.49	±0.03
3	Alfalfa hay field	1.39	±0.03	1.48	±0.03
4	Bluegrass sod orchard	1.26	±0.03	1.37	±0.01
5	Woodlot	0.995	±0.02	....	.

Volume weight

Each plot was sampled by means of a volume weight tube 12 inches long and 2.5 inches in diameter. The first and second 3-inch layers were taken separately and, in each case, 10 cores were included in the average presented in table 1. The woodlot soil has the lowest volume weight and is therefore the most porous site. In the order of decreasing porosity the other plots were bluegrass sod, alfalfa meadow, alfalfa orchard, and, the most compact, the plot growing two covers annually. The growing of two annual cover crops together with the preparation necessary at seedtime has permitted considerable destruction of the physical structure as shown by the high volume weight. Noteworthy is the effect of the bluegrass sod in bringing about a greater porosity, especially in the first 3 inches.

Organic matter

Total organic matter was determined in triplicate, upon the samples taken for volume weight determination, by the Shollenberger (11,12) method as

modified by Allison (2) and Tiulin (14). Table 2 shows that the bluegrass sod has been particularly effective in maintaining a high organic content in the upper 3-inch layer. The alfalfa sod is next in order among the orchard plots and contains almost as much in the second 3-inch layer as in the first. The cultivated and cover-cropped plot is significantly lower in organic content. Alderfer and Merkle (1), Burr and Russel (7), Jenny (8), Browning (6), Peele (9, 10), Smith (13), Baver (4, 5), and Baver and Harper (3) all attach great significance to the influence of organic matter upon the development of good soil structure. As will be shown later, this study confirms this opinion.

Aggregate stability and probable permeability

By the method proposed by Alderfer and Merkle (1), the stability index and the probable permeability of each plot were determined upon the samples taken for volume weight determination. Alderfer and Merkle point out that

TABLE 2

Organic content (C × 1.724) of the first and second 3-inch layers of plots under different systems of soil management

PLOT	1ST 3-INCH LAYER	2ND 3-INCH LAYER
	per cent	*per cent*
1	2.62	2.40
2	3.03	2.91
3	3.17	2.98
4	5.02	3.14
5	5.21	...

both the stability and the size of the natural granules are important in determining the size of the pores and their tendency to remain open for infiltration. These properties are expressed as single values, the larger the value the greater the manifestation of the property. The averages of closely agreeing triplicate analyses and the data from which these values were obtained are shown graphically in figures 1–9. In the first 3-inch layer the forest sample has the greatest probable permeability and stability of granules, as a result of many years of development and protection under the litter and humus layers. The bluegrass sod produced a very desirable structure in the upper 3-inch layer, but the second 3-inch layer was not found to be so good as that under the alfalfa cover, indicating that structure is produced by roots and that the deeper-rooted alfalfa causes granulation to extend deeper into the profile. The plot which is cultivated twice yearly and sown to annual covers is decidedly the poorest structurally in both layers, indicating that loss of organic matter and exposure to beating rains before the cover crop becomes established bring about considerable structural breakdown.

Of the orchard soils, the bluegrass sod, which will be shown later to have

the best infiltration capacity, has decidedly the best permeability in its upper 3-inch layer, suggesting that for this soil at least the surface layer is the most important in its effect upon the intake of rains.

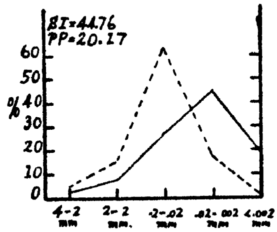

FIG. 1. Cultivated orchard 1st 3".

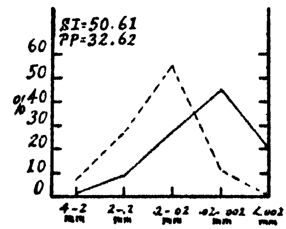

FIG. 2. Alfalfa sod orchard 1st 3".

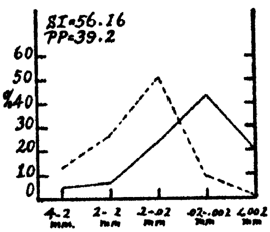

FIG. 3. Alfalfa hay field 1st 3".

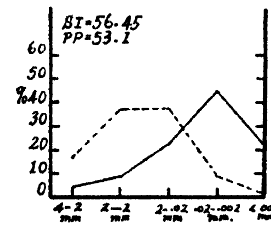

FIG. 4. Bluegrass sod orchard 1st 3".

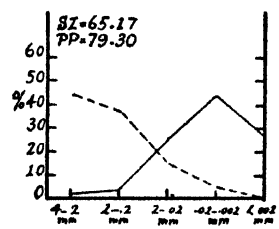

FIG. 5. Woodlot 1st 3".

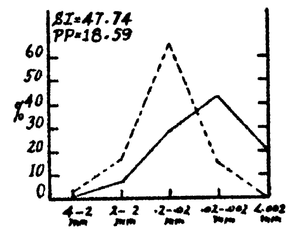

FIG. 6. Cultivated orchard 2nd 3".

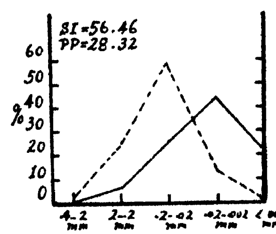

FIG. 7. Alfalfa sod orchard 2nd 3".

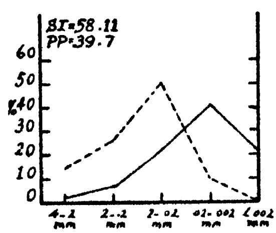

FIG. 8. Alfalfa hay field 2nd 3".

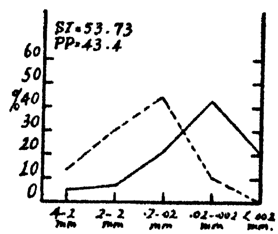

FIG. 9. Bluegrass sod orchard 2nd 3".

FIGS. 1–9. MECHANICAL AND AGGREGATE ANALYSES OF SOILS OF PLOTS 1–5, FIRST 3-INCH LAYER, AND OF PLOTS 1–4, SECOND 3-INCH LAYER

Broken line, aggregate analysis; solid line, mechanical analysis; S. I., stability index; P. P. probable permeability

Infiltration

The infiltration capacity was determined by the use of an irrigator consisting of a "Flaring Rose" sprinkler head *H* (fig. 10) with six openings, adjusted to deliver water at the rate of approximately 3 inches an hour over the area measured, and supported $3\frac{1}{2}$ feet above the ground. Pressure was supplied from a 5-gallon water supply bottle *B* held $5\frac{1}{2}$ feet above the ground. A piece of galvanized sheet iron 6 inches wide was bent to form a rectangular frame *F* 2 feet by 1 foot. The upper 4 inches of the wall of this frame were stiffened from the outside by boards 4 inches wide. This iron frame was

sunk 2 inches into the ground to delimit a 2- by 1-foot area for study. Oiled canvas *C* was fitted to the edge of the frame and extended outward to collect all water that fell outside the study area and to deliver it to vessel *Y*. A drainage pipe *P*, fitted to the frame at the ground level, conveyed the runoff

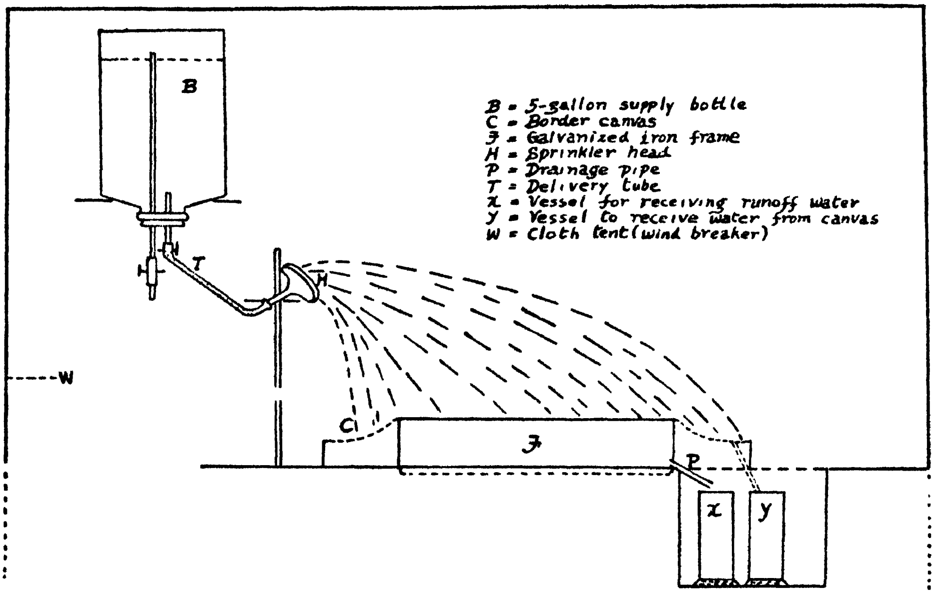

FIG. 10. DIAGRAM OF THE SPRINKLING APPARATUS

TABLE 3

Infiltration rates in soil of experimental plots during the second application of water at the rate of 3 inches an hour for 55 minutes

PLOT	NUMBER OF SITES	INFILTRATION	STANDARD ERROR
		inches/hour	
1	8	1.11	±0.11
2	8	2.11	±0.23
3	8	2.47	±0.16
4	5	2.82	±0.14
5	5	2.97	±0.004

water which did not soak into the soil, and emptied it into vessel *X*, thus eliminating the effect of inundation. A cloth tent was used as a windbreaker *W*.

From the amount of water applied and the runoff from the area enclosed, it was possible to calculate the rate of infiltration in inches per hour. Two applications were made 24 hours apart. The first application was employed to saturate the soil thoroughly. Only the rates of infiltration of the second application, which was made 24 hours after the first, are reported in this

study, as these were assumed to represent the infiltration capacity of a soil which had been recently saturated and the excess allowed to drain off.

Five to eight sites were chosen on each plot with a view to avoiding tree

TABLE 4

Approximate depth of moisture penetration by natural rain in soils of experimental plots

DATE OF RAIN	DATE OF SAMPLING	RAINFALL			SAMPLE DEPTH	MOISTURE CONTENT		
		Average amount	Average intensity	Maximum intensity		Plot 1	Plot 4	Plot 2
		in /hr.	*in /hr*	*in./hr.*	*inches*	*per cent*	*per cent*	*per cent*
July 10	July 11	0.26	0.52	0.96	1	21.0		29.7
					2	21.5		25.0
					3	20.3		22.2
					4	18.6		22.8
					5	18.0		23.4
					6	18.7		25.0
July 11, 12	July 13	0.68	0.12	1.44	1	23.5	30.0	31.8
					2	23.7	29.6	31.9
					3	23.4	27.9	30.8
					4	24.4	26.5	27.6
					5	23.6	26.6	28.5
					6	23.4	27.6	28.3
					7	23.9	27.7	28.9
					8	24.1	27.3	29.8
					9	23.2*	27.4	29.3
					10	22.3	24.9*	27.7*
					11	20.5	22.6	24.8
					12	20.3	23.6	25.9
					13	19.0	21.6	22.4
					14	19.4	21.6	22.4
					15	19.7	21.2	22.0
July 23	July 24	0.75	0.43	3.00	1	21.2	27.4	25.5
					2	20.0	26.4	25.8
					3	21.3	25.7	25.2
					4	20.4	25.8	26.0
					5	17.5	26.5	25.6
					6	19.0	25.5	25.1
					7	19.3	25.6	25.8
					8	18.7*	24.4	26.8
					9	17.3	25.0	25.3
					10	18.2	23.8*	23.5*
					11	16.2	24.2	21.8
					12	17.5	21.6	19.8
					13	17.5	20.3	19.8
					14	18.0	20.3	20.9
					15	17.8	18.5	19.1

* The level at which subsoil begins.

TABLE 4—*Concluded*

DATE OF RAIN	DATE OF SAMPLING	RAINFALL			SAMPLE DEPTH	MOISTURE CONTENT		
		Average amount	Average intensity	Maximum intensity		Plot 1	Plot 4	Plot 2
		in./hr.	*in./hr.*	*in./hr.*	*inches*	*per cent*	*per cent*	*per cent*
July 24		0.20	0.60	0.80	1	16.6	25.0	29.8
July 26		0.20	0.80	1.44	2	17.5	24.9	28.5
July 27		0.10	0.05	0.24	3	17.7	24.1	27.1
July 28		0.40	0.53	1.68	4	16.1	23.8	27.5
	July 29				5	16.1	24.3	27.5
					6	17.6	23.9	28.0
					7	18.3	23.4	27.9
					8	16.6	25.6	27.6
					9	16.8*	25.0	25.8
					10	16.8	24.3*	23.3*
					11	15.7	23.7	22.8
					12	16.6	22.4	22.1
					13	17.4	20.5	21.3
					14	17.5	19.4	20.8
					15	16.9	18.3	21.1

roots and wheel tracks as much as possible. The vegetation was cut close to the ground to eliminate the canopy effect. Table 3 records the mean infiltration capacity rates in inches per hour for the plots under study.

Moisture content and penetration

If the covers that have been used have altered the structure and therefore the amount of infiltration and runoff, then that treatment which allows the greatest infiltration should gradually increase the total moisture content in the entire soil mantle. The effect should be cumulative from year to year. In the period from 1926 to 1940 a measurable difference might be expected. That such difference occurs is shown by moisture determinations made on four occasions on the three orchard plots. Samples were taken with a soil tube at 1-inch intervals to a total depth of 15 inches and 24 hours after natural rain. The data are presented in table 4. At corresponding levels the cultivated plot contains 1 to 8 per cent less moisture than either the bluegrass sod plot or the alfalfa sod plot. These data would appear to indicate that the increased infiltration produced by the perennial covers has more than counterbalanced the increased demand for moisture made by the cover crop.

The data also indicate a greater depth of moisture penetration in the sod plots than in the cultivated plot. When the intensity of rainfall was low and when the total amount of rain was small, however, the penetration was shallower in the sod plots because of greater surface loss through evaporation of the intercepted portion of the precipitation.

Runoff and erosion losses

As has been indicated, catch basins were installed in 1935 in each plot to study soil and water losses under the different systems of soil management. The soil and water losses for 1936–1939 inclusive are presented in table 5. They show that the bluegrass sod has lost almost no soil or water; the alfalfa sod, which contains some volunteer bluegrass, has also suffered only slight losses, whereas the cultivated orchard with two annual cover crops has lost about 5 per cent of the rainfall and more than 8000 pounds of soil in spite of the fact that the total amount of cultivation seldom exceeded 2 weeks in any one year. Most of these losses were caused by heavy storms coming when the ground was bare.

SUMMARY AND CONCLUSIONS

A study of experimental orchard plots under different systems of soil management and of annual and perennial cover crops was made to determine what

TABLE 5

*Soil and water losses, 1936–1939 inclusive, from orchard plots under different systems of soil management**

PLOT	SOIL LOSS	RAINFALL
	lbs./A.	*per cent*
1	8,362.8	4.6
2	43.8	0.1
4	23.2	0.05

* Data taken from mimeographed report of N. F. Farris and associates, on the experimental plots of the Soil Conservation Experiment Station, State College, Pennsylvania, 1940.

effect, if any, these treatments might have upon the physical characteristics of soil and its moisture relationships. The findings summarized in figure 11 are in agreement in showing that:

Different soil covers produced marked changes in organic content and in physical properties which alter the infiltration capacity and moisture status of the soil mantle.

Cultivation in the fall and spring with an annual cover crop of rye sown in the fall and millet in the spring permitted soil deterioration, as evidenced by a reduction in the organic content, the granule stability, and the probable permeability. A more compact, easily dispersed surface layer resulted, giving rise to poorer infiltration and greater erosion and runoff.

Alfalfa sod harrowed only in the spring resulted in higher organic content, better structure, increased infiltration, and decreased runoff and erosion.

A permanent bluegrass sod harrowed each spring gave the highest organic content and the greatest structural stability and permeability in the surface 3-inch layer, which resulted in excellent infiltration and almost no runoff and erosion.

The cumulative effects of these treatments from 1926–1940 have resulted in a better moisture status in the entire soil mantle where perennial cover crops were used.

There is a close correlation between changes brought about in the physical properties and the actual measurements of moisture infiltration, runoff, and moisture content in the profile.

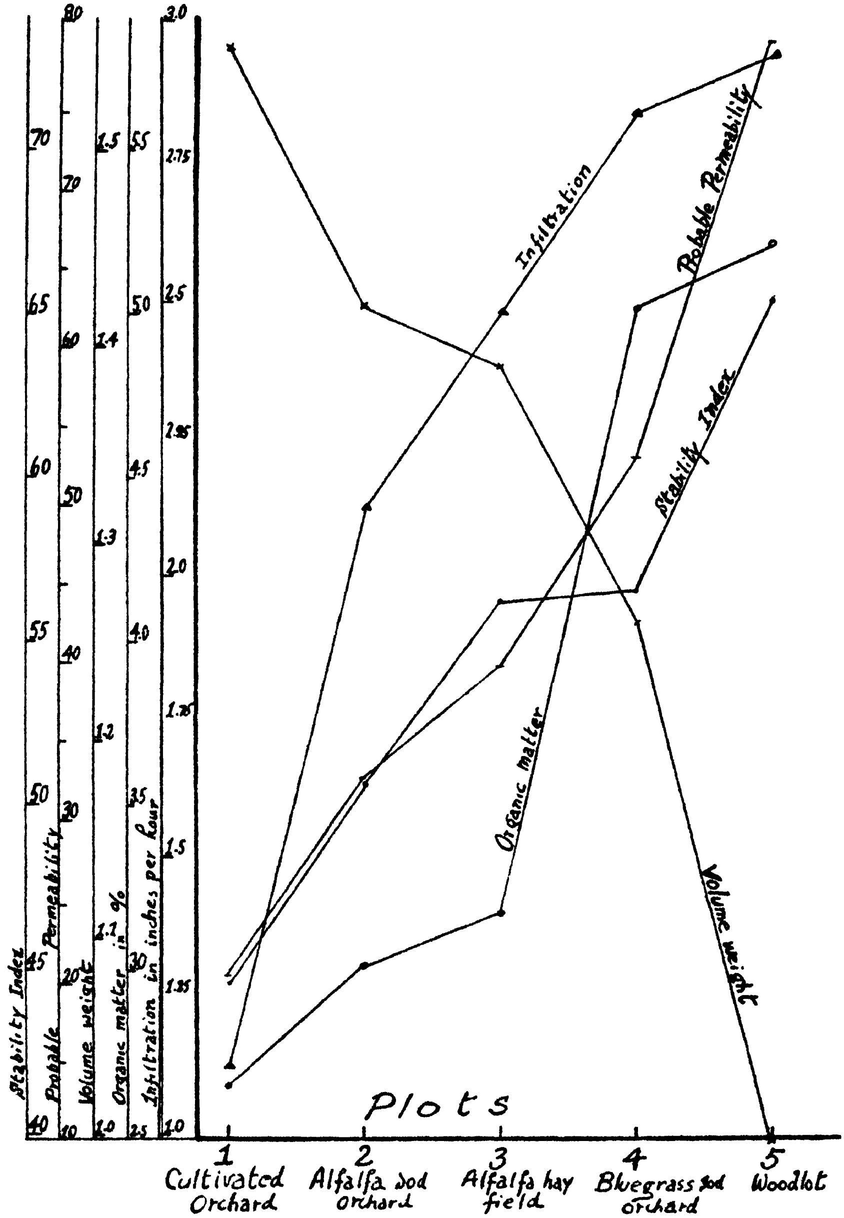

FIG. 11. CORRELATION OF PHYSICAL PROPERTIES WITH INFILTRATION RATES OF SOILS OF PLOTS 1–5

Evidently the exposure of the soil to rainfall and drying during the fall and spring preparations, together with the time required for the annual cover crops to become effective, has resulted in physical deterioration as compared with conditions found under the perennial covers.

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COMPARATIVE STUDY OF THE CALCIUM-BORON METABOLISM OF REPRESENTATIVE DICOTS AND MONOCOTS[1]

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During the last few years experimental data have established the fact that some agricultural species of dicots and monocots are unlike in their quantitative requirement of nutrient ions (5, 6, 9). In this connection Shive and Marsh and Shive have employed a general procedure which includes investigations of microscopic structure of the plant and the quantitative chemical and microchemical study of the plant tissues as criteria for comparison of different plant species. Details of the procedure are given in recent studies of corn and faba bean (5, 9). In order to facilitate a comparison of the two plant groups, dicots and monocots, with respect to boron and calcium metabolism, the same general plan has been followed in this work. A brief resume of this plan is here given in reference to the present experiments.

PLAN OF EXPERIMENT

Five series of sand cultures for each of the dicots, tobacco (Kentucky White Burley variety number 5) and faba bean (*Vicia faba*), and for each of the monocots, corn (Croshaws' strain of Reeds' yellow dent) and oats, were prepared (5). Consecutive series with duplicate cultures were conducted for each type of plant, each series being supplied with culture solution by the continuous flow drip method (7). The boron and the calcium treatments are indicated in table 1 and are designated in table 2 for each of the five series as deficient, optimum, or toxic, since in the respective series so indicated the plants exhibited symptoms usually associated with boron or calcium deficiency or boron toxicity or developed optimum growth (4). All cultures were supplied with the complete culture solution containing all the necessary trace elements (8) until the plants were large and vigorous. This period of growth was not the same for all the species of plants investigated or even for the same species in consecutive series. A longer period was required for the dicots to become well established than for the monocots. In general, the monocots were supplied with the complete solution for 7 to 14 days before the boron and calcium solutions given in table 1 were added; the corresponding period for dicots was 21 to 28 days. These preliminary periods were followed by relatively short

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periods of treatment with the solution containing the boron and calcium. These treatment periods were shorter for the dicots than for the monocots. Invariably, monocots, because they have a lower boron requirement than dicots, develop symptoms of deficiency less rapidly than do dicots. All the

TABLE 1

Solutions used with series of dicots and monocots grown in sand culture

SERIES	MOLAR CONCENTRATIONS OF MAJOR SALTS					TRACE ELEMENTS		
	KH_2PO_4	$Ca(NO_3)_2$	$NaNO_3$	$MgSO_4$	$(NH_4)_2SO_4$	Dicots	Monocots	Dicots and monocots
						Boron	Boron	Fe, Mn, Zn
						p.p.m.	*p.p.m.*	*p.p.m.*
1	0.0023	.. ...	0.0090	0.0023	0.0007	0.00	0.00	0.25
2	0.0023	.. ...	0.0090	0.0023	0.0007	0.50	0.25	0.25
3	0.0023	0.0045	......	0.0023	0.0007	0.00	0.00	0.25
4	0.0023	0.0045	......	0.0023	0.0007	0.1 and 0.5	0.1 and 0.25	0.25
5	0.0023	0.0045	......	0.0023	0.0007	15.00	5.00	0.25

TABLE 2

Average quantities in milligrams, of total and soluble calcium and boron per gram of dry tissue of the dicots, tobacco and faba bean, and of the monocots, corn and oats

SERIES		DICOTS				MONOCOTS			
		Total calcium	Soluble calcium	Total boron	Soluble boron	Total calcium	Soluble calcium	Total boron	Soluble boron
1	Deficient boron Deficient calcium	8.00	0.50	0.0090	0.0001	2.00	0.15	0.0016	0.0009
2	Optimum boron Deficient calcium	6.03	0.77	0.0240	0.0085	2.05	0.65	0.0080	0.0064
3	Deficient boron Optimum calcium	18.00	2.98	0.0077	0.0005	7.60	2.15	0.0020	0.0013
4	Optimum boron Optimum calcium	19.29	4.44	0.0182	0.0052	7.77	2.70	0.0066	0.0053
5	Toxic boron Optimum calcium	17.80	4.40	0.0590	0.019	7.35	4.1	0.0245	0.0211

plants of the respective series were harvested when the boron or calcium deficiency and toxicity symptoms had developed noticeably (4). In corn and oat plants no signs of boron or calcium deficiency were observable for about 10 days after treatments were begun, whereas in tobacco and faba bean symptoms were readily observable within 3 or 4 days. This difference between the

two types of plants suggests that the dicots require more boron or calcium in the substrate than do the monocots (9).

Calcium in the plant tissues was determined quantitatively by the micromethod of the Association of Official Agricultural Chemists (1, 5, 6, 9); boron, by the Berger and Truog colorimetric method (2, 5, 9). Procedures for the determination of crystals of calcium and of boron in the plant tissue ash or within the plant tissues are adaptations of microchemical methods described by Chamot and Mason (3, 5, 9).

CHEMICAL INVESTIGATIONS

The quantitative chemical analyses of total and soluble calcium and boron in the plant tissues are given in table 2.

A comparison of the data from the calcium-deficient cultures (table 2) strongly suggests that for both dicots and monocots, optimum boron concentrations within the substrate, as in series 2, tend to maintain in a soluble condition a higher percentage of the calcium previously acquired by the plant, than that maintained in the absence of boron from the substrate, as in series 1 (5, 9).

The data for series 3, 4, and 5 (table 2), in which optimum calcium concentrations were supplied continuously to the cultures that were receiving, respectively, deficient, optimum, and toxic boron concentrations in the substrate, show that the total calcium concentration per gram of dry tissue is fairly uniform for the dicots as well as for the monocots; on the other hand, dicot tissue contains more than twice as much calcium per gram as does monocot tissue (9). The data indicate further that the percentage of soluble calcium is directly related to the percentage of soluble boron in the plants (9).

MICROCHEMICAL INVESTIGATIONS

The crystal counts for total and soluble calcium and for total and soluble boron within the plant tissues were in general agreement with the quantitative determinations (3, 5, 9).

DISCUSSION

For normal growth, the dicots require higher concentrations of boron in the substrate than do the monocots (9). The reason is that a higher percentage of the accumulated boron remains soluble in the monocots than in the dicots. This soluble boron acts directly or indirectly to maintain calcium in the soluble and therefore in an active state. In both the dicots and the monocots, high concentrations of boron in the substrate result in relatively high concentrations of boron in the plant tissues and vice versa.

A contributing factor to the general phenomenon of the difference in boron requirement between dicots and monocots may be the difference in the morphological make-up of the two types of plants. In the species here investigated the mass of active meristematic tissue, relative to the total tissue mass, is much

greater in the dicots than in the monocots, and because of this a relatively high boron requirement in the dicots and a correspondingly lower one in the monocots may be directly associated with the maintenance of the normal status of calcium metabolism. This, however, is only a suggestion requiring substantiation by quantitative experimental evidence.

SUMMARY

In a comparative study of their calcium-boron metabolism, two dicots, tobacco and faba bean, and two monocots, corn and oats, were grown in sand supplied by the continuous flow method with five series of culture solutions containing various quantities of boron and calcium considered as deficient, optimum, or toxic. Observations on the growth of these plants and quantitative chemical and microchemical examination of the tissues led to the following conclusions:

The optimum boron requirement is greater for the dicots than for the monocots.

Both dicots and monocots grow normally only within the optimum range of boron concentration of the tissues. The substrate must supply this optimum amount of boron or else the plants show pathological symptoms of deficiency or toxicity.

For both dicots and monocots, the presence of adequate available boron within the plant tends to maintain the calcium, previously acquired, in an available condition, even though no fresh supply of calcium is provided in the substrate.

The boron content of the substrate, within certain limits, does not influence significantly the calcium absorption rates of either the dicots or the monocots.

The soluble calcium in both the monocot and the dicot tissues is determined not by the total calcium of the plants, but by the boron content, which in turn, is determined by the boron content of the substrate.

A relatively very large proportion of the boron in the monocot is in soluble form, in comparison with that in the dicot.

For both monocots and dicots, the proportion of soluble boron is directly related to the total boron in the plants and to the boron content of the substrate.

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STABILITY OF CLAY SOILS

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The use of soil moisture characteristics as indicative of soil stability has already been described (1).[2] The object of the present paper is to show the application of the method in an attempt to solve some urgent present-day problems. For details of the method, the paper referred to may be consulted. Briefly, the progressive disintegration of the soil caused by one or more cycles of a defined weathering process is studied. To do this, it is clearly necessary that the analytical methods used should not themselves cause any disintegration which would mask the effects of weathering. The method adopted here is to investigate the pore-size distribution of the intercrumb pore space by means of soil moisture characteristics (i.e., curves relating soil moisture content to pressure deficiency or suction), taken before and after the weathering cycle. A concentration of pores about an effective pore radius r is shown by the presence of a peak in the differential of the moisture characteristic at a pressure deficiency p related to r by the equation

$$p = 2T/r$$

where T is the surface tension of the soil water. It is desirable to have a pronounced peak in the initial curves before weathering, since subsequent modifications due to weathering are thereby more easily interpreted, and this is assured by working with a crumb fraction initially of limited size range. The fraction used throughout the present work consists of crumbs of dry soil passing the 2-mm. but resting on the 1-mm. sieve (the holes in the sieves being circular). Disintegration of such a crumb fraction in general results in diminution of intercrumb pore size accompanied by widening of the range of pore sizes and reduced prominence of the initial pore group. This is shown in the

[1] I wish to thank F. L. Engledow, university professor, and D. H. Findlay, Executive Officer of the Leicestershire War Agricultural Executive Committee, through whose good offices and interest the profiles of the Lias clays were obtained; H. H. Nicholson, who collected the interesting sample of London clay and made some helpful suggestions in presenting the material of the paper; and T. Deighton, but for whose developmental work the study would have taken several months longer to complete.

[2] Since this paper was written, the author noticed that E. W. Russell, in his survey of soil structure work up to 1937 (5), mentioned briefly the possibility of using pore-space measurements, although at that time there was little work to record, and that little had not been developed very far. For a summary of conclusions as to soil structure and stability derived from aggregate analysis methods, and for a bibliography covering this field, Russell's paper may be consulted.

moisture characteristics (or rather the differentials of these) by a broadening and lowering of the peak together with a shift of the maximum toward a higher pressure deficiency. The extent of this change is a measure of the disintegration due to the intervening cycle of weathering and therefore of the instability of the soil.

SCOPE OF EXPERIMENTS

The present demands upon British agriculture for increased production require the ploughing of millions of acres of grassland. Much of this is heavy, difficultly worked land which went out of arable cultivation during the years of the agricultural depression, the drainage of this land then being neglected as an unprofitable undertaking. In addition, much heavy clay land lies in traditional grazing country, and drainage has been neglected, partly, perhaps, because the evils of poor drainage are less obvious to the eye in grassland than in arable land, but also because there is a body of opinion among graziers, well founded or not, that draining reduces stock-carrying power at the height of the summer when it is most wanted, and is therefore undesirable. As a result, there is much clay land to be drained at a time when labor and materials are becoming increasingly scarce. Mole draining, because of its low requirements of labor and materials and because of its speed of execution, quite apart from its intrinsic merits, is the obvious solution of the problem and is so recognized by the Government.

Unfortunately, in many parts of the country where mole draining is indicated, this operation has not been widely practiced in the past. Hence there is little experience of the operation itself and little local knowledge of the suitability of the prevailing soils for carrying moles with any reasonable expectation of life. Senility of mole drains in suitable soil is recognized to be due to the piecemeal collapse of the walls as a result of the annual wetting and drying cycle (3), rather than to silting during the drainage season itself. Hence there would appear to be scope for the stability analysis outlined above to indicate broadly those soils which are suitable for mole draining, by measuring the stability of soils to the wetting and drying cycle. Records of single mole drains in grassland obtained by the author during the last few years, using automatically recording flow meters, show several instances of flow in a single channel reaching or exceeding 15 liters a minute (about 200 gallons an hour), a rate which would fully tax a smooth-walled channel of 1.5-inch diameter and fall of one in a hundred. To cope with these considerable rates of flow clearly requires an unobstructed mole channel, and if this requirement is to be satisfied for a number of years soil stability at the depth of moling must obviously be high. These requirements of stability apply also to a lesser extent throughout the profile above the mole channel, since closure of the mole slit and its accompanying fissures by breakdown of structure in the upper horizons may effectually seal off the mole channel from surface water. For this reason, stability studies are preferably made throughout

the soil profile. It is not suggested that laboratory experiments of the type described can, in their present stage of development, provide all the guidance desirable; actual mole draining experiment or experience is, of course, to be preferred. But if a decision must be taken in the absence of such experience, it is believed that work of this kind may prevent many cases of mole failure.

EXPERIMENTAL PROCEDURE

It is generally sufficient to allow for two successive cycles of wetting and drying; therefore, three samples of each soil are required. The moisture limits adopted were air-dryness and saturation, and the cycles were conveniently carried out in evaporating basins of about 100-cc. capacity, three of which were allotted to each soil. In the three basins were placed equal volumes of crumbs, rendered as nearly as possible identical by suitable sampling from the bulk. Two of the samples were then covered with distilled water, the third was placed in the Büchner funnel of an apparatus of the Haines type (2), and all were allowed to soak for 24 hours. At the end of this period excess water was drained off the soils in the basins, the soils then being left to dry slowly at room temperature and humidity, while excess free water was removed from the Büchner funnel and the moisture characteristic taken for the soil crumbs once wetted. Of the two air-dry samples remaining in the basins, one was again saturated and left to soak for 24 hours while one was removed to the Büchner funnel, the moisture characteristic being then obtained after one cycle of weathering. If necessary, the third sample was finally used for obtaining the moisture characteristic after two cycles of weathering. It was usually found that the cake of dried crumbs was easily removed from the basin without mechanical disintegration, except for a rim of crust which had to be pried off. Any dust produced by this process was blown away before the crumbs were placed in the funnel. When in the funnel and covered with water, the cake of weathered crumbs readily collapsed, and a little tapping of the funnel sufficed to level the surface and to drive out most of the trapped air without contributing appreciably to the disintegration. The volume of soil chosen was sufficient to produce a layer about 1 cm. thick in the funnel, this thickness being sufficient to ensure that the pore size distribution fairly represented that in the bulk, while variations of pressure deficiency through the thickness were not sufficient to complicate the moisture characteristics. The volume of the crumbs when wet was found by a separate experiment, and pore volume was expressed as a percentage of the apparent volume of wet crumbs.

Since the crumb separation was carried out with dry soil and the moisture characteristic was taken with initially saturated soil, it is impossible, of course, to produce a characteristic for soil which has suffered no weathering at all. The initial curves I in the diagrams in this paper are for crumbs which have been once wetted after dry sifting, curves II, described as "after one cycle of weathering," really correspond to the sequence wetting-drying-rewetting,

and so on. To anticipate the results, this undoubtedly accounts for the difference between the initial curves for soils of different stability. There is no reason why the same mechanical sifting operation on different soils should produce crumb fractions of identical size distribution, although the difference can never be large when the range of sizes is as limited as that adopted here. No difference between the crumb fractions of the various soils was, however, obvious to the eye, and therefore truly unweathered crumbs of all soils might be expected to give substantially similar moisture characteristics. Certainly it can be said that where the "initial" characteristic shows only a very unobtrusive peak or none at all, as in Middle Lias subsoil, the weathering, due to the first wetting after dry sifting, was obvious to the eye. It does not seem worth while to indulge in troublesome wet sifting in order to start with similar fractions in all soils, since our measure of stability is obtained by comparison between characteristics before and after the controlled weathering of the same soil, whatever the initial characteristic may be like. In fact, the separation of a crumb fraction serves only to provide a marked peak in the initial characteristic, and provided this is achieved, it does not matter much what sort of a peak it is; the precise nature of the crumb fraction is of no importance.

EXPERIMENTAL RESULTS

Soil profiles were obtained from the Upper, Middle, and Lower Lias formations of Leicestershire, each profile being sampled in 3-inch layers down to a depth of 24 inches. The mechanical analyses (the I.S.S.S. classification) and other relevant information are given in table 1.

It will be seen that the clay percentage in the Lower and Middle Lias has no particular trend throughout the profile, but in the Upper Lias a distinct maximum is evident at the 9–12-inch depth and a sharp decrease at the 21–24-inch depth. All three profiles were from old grassland and show the development of the characteristic organic matter profile. The textures of both the Upper and Lower Lias were designated as clay, with little to choose between the two (although the mechanical analyses show the former to be the more silty). The Middle Lias, on the other hand, was no heavier than a light to medium loam. The orange mottling so characteristic of poor drainage conditions was very pronounced in the Upper and Middle Lias, but less so in the Lower Lias.

The moisture characteristics of these soils are not shown, since the inter-crumb pore group and its modification due to weathering are more clearly seen in the differentials of these curves. These differentials are shown in figures 1 to 3 for the Upper, Middle, and Lower Lias respectively; those soils showing the greatest modification by weathering are the least stable. The most pronounced feature of all three soils is the marked falling off in stability with increasing depth. Table 1 indicates that the organic matter is the only item that shows marked variation with depth, parallel with the stability vari-

ation, in the profiles. It is almost unavoidable, even if not strictly logical, to conclude that this is by far the most important single factor in determining stability of the surface soil, the more so because the order of stability, namely, Upper > Middle > Lower, is the same as the order of organic matter

TABLE 1

Analyses of Upper, Middle, and Lower Lias soil profiles

DEPTH	CLAY	SILT	FINE SAND	COARSE SAND	$CaCO_3$	ORGANIC MATTER*	LOSS ON SOLUTION	H_2O†	pH
inches	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
Upper Lias									
0– 3	51.50	20.00	4.42	1.15	0	17.78	4.80	6.30	4.91
3– 6	55.00	18.00	3.99	0.86	0	8.41	5.20	6.30	5.07
6– 9	58.50	21.00	4.65	0.85	0	5.61	2.26	6.10	5.27
9–12	62.75	21.00	4.31	0.71	0	2.98	1.86	5.39	5.49
12–15	59.75	26.50	4.32	1.31	0	2.59	1.54	5.27	5.58
15–18	56.25	27.00	5.74	1.61	0	2.08	1.10	4.95	5.78
18–21	52.00	29.00	10.31	3.30	0	1.44	1.10	4.39	6.02
21–24	46.50	32.75	10.09	4.99	0	1.35	0.91	4.48	6.23
Middle Lias									
0– 3	27.25	23.25	23.93	3.95	0.04	10.93	4.05	5.50	6.41
3– 6	28.00	24.25	26.54	6.95	0	3.98	3.24	3.90	6.18
6– 9	28.50	26.75	29.46	4.60	0	2.96	2.20	3.40	6.28
9–12	29.00	27.75	30.20	4.15	0	2.20	1.95	3.20	6.33
12–15	31.00	24.75	35.19	1.83	0	1.18	1.40	2.60	6.21
15–18	28.00	22.00	40.12	2.27	0	0.86	1.25	2.70	5.88
18–21	30.50	21.50	38.33	2.23	0	0.60	1.35	2.70	5.18
21–24	28.50	25.00	39.04	3.32	0	0.65	1.05	3.00	5.26
Lower Lias									
0– 3	53.50	10.25	3.45	3.80	1.23	8.70	4.85	12.60	7.68
3– 6	59.50	9.50	3.79	3.60	4.47	4.53	4.10	8.80	7.98
6– 9	58.75	13.50	3.28	2.55	4.44	2.99	3.55	9.80	8.00
9–12	60.50	12.50	3.02	2.50	2.44	2.85	2.70	9.30	8.00
12–15	65.25	13.75	3.55	3.60	0.35	1.83	1.60	8.00	8.02
15–18	57.00	15.75	7.52	8.80	0.21	1.78	2.10	6.80	8.00
18–21	54.75	12.00	8.74	10.90	0.74	1.78	2.46	7.35	7.85
21–24	61.25	11.00	6.84	7.00	0.51	1.83	1.97	7.55	8.02

* O.M. = 1.73 × organic carbon by the Walkley-Black method.

† Content of air-dry soil.

content. On the other hand, the order of clay content is Lower > Upper > Middle, and is clearly virtually irrelevant. The clay content of the Middle Lias is so inadequate to confer stability that, below a depth of 12 inches, where organic matter is negligible, stability is not observable. Stability of

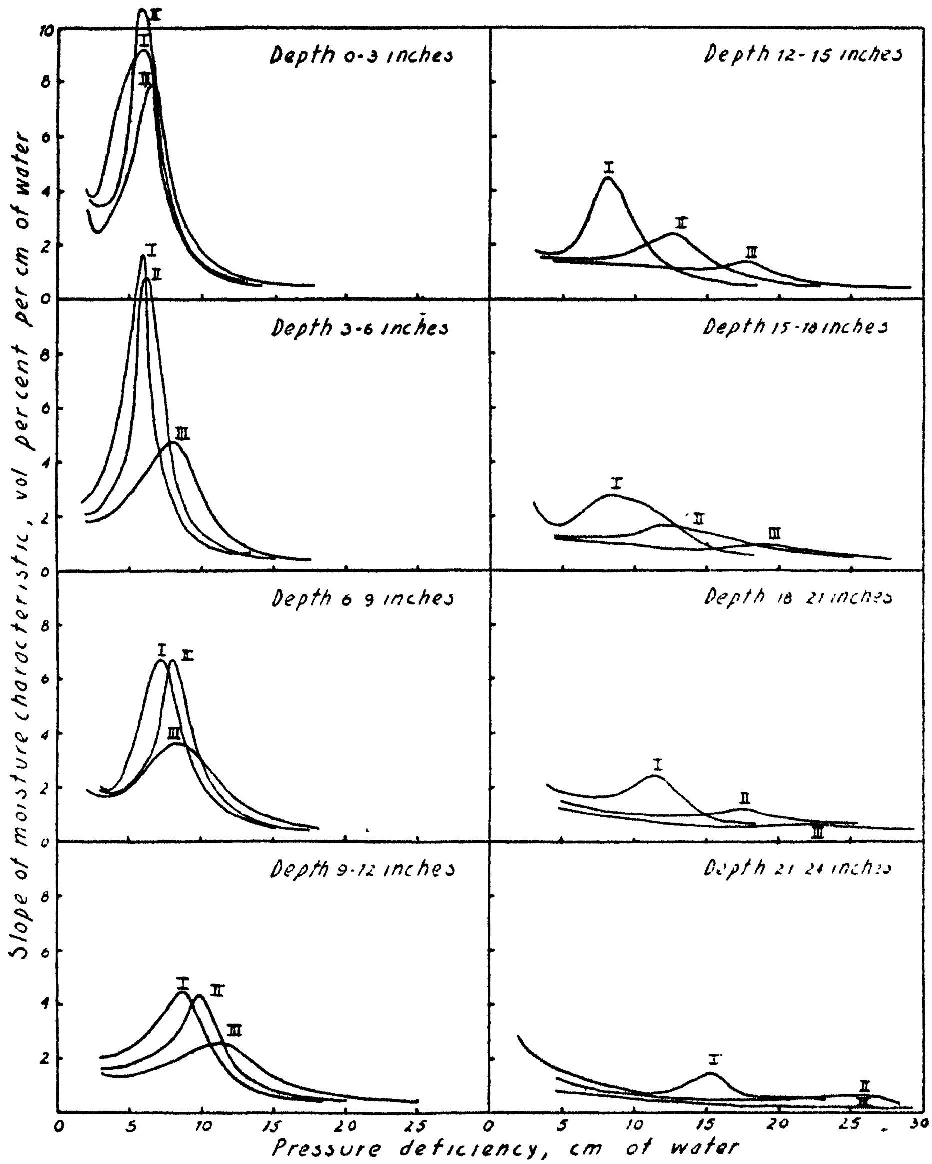

FIG. 1. DIFFERENTIALS OF MOISTURE CHARACTERISTICS FOR UPPER LIAS CLAY AT VARIOUS DEPTHS, BEFORE AND AFTER ARTIFICIAL WEATHERING

Curve I, initial characteristic; curve II, characteristic after one cycle of weathering; curve III, characteristic after two cycles of weathering. The peak in each curve corresponds to the intercrumb pore group of the 1–2-mm. crumb fraction. The degree of modification of this peak by weathering is an indication of the instability of the soil.

both the Upper and Lower Lias is considerable, the former being the more stable at all depths except 21–24 inches. Table 1 shows a pronounced lighten-

ing with depth of the Upper Lias from 12–24 inches, and it may be that at 24 inches the reduction of clay content is sufficient to account for the falling off

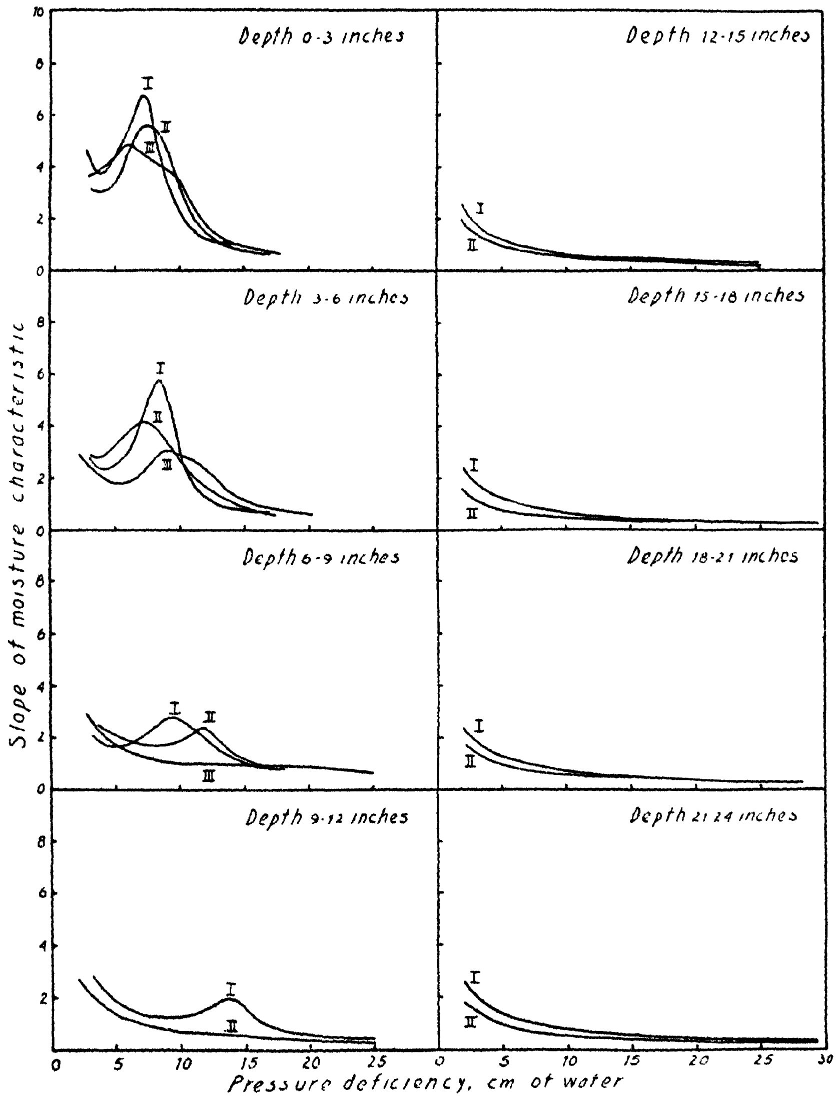

FIG. 2. DIFFERENTIALS OF MOISTURE CHARACTERISTICS FOR MIDDLE LIAS CLAY AT VARIOUS DEPTHS, BEFORE AND AFTER ARTIFICIAL WEATHERING

Curves I—III, as in figure 1

in stability. The lime status of the two soils is matter for comment. It is generally considered that a good lime status, consequent upon adequate free calcium carbonate, makes for good stability as shown by excellence of tilth,

but it will be observed that here the Lower Lias has a quite definite, if not ample, reserve of calcium carbonate and is well on the alkaline side of neu-

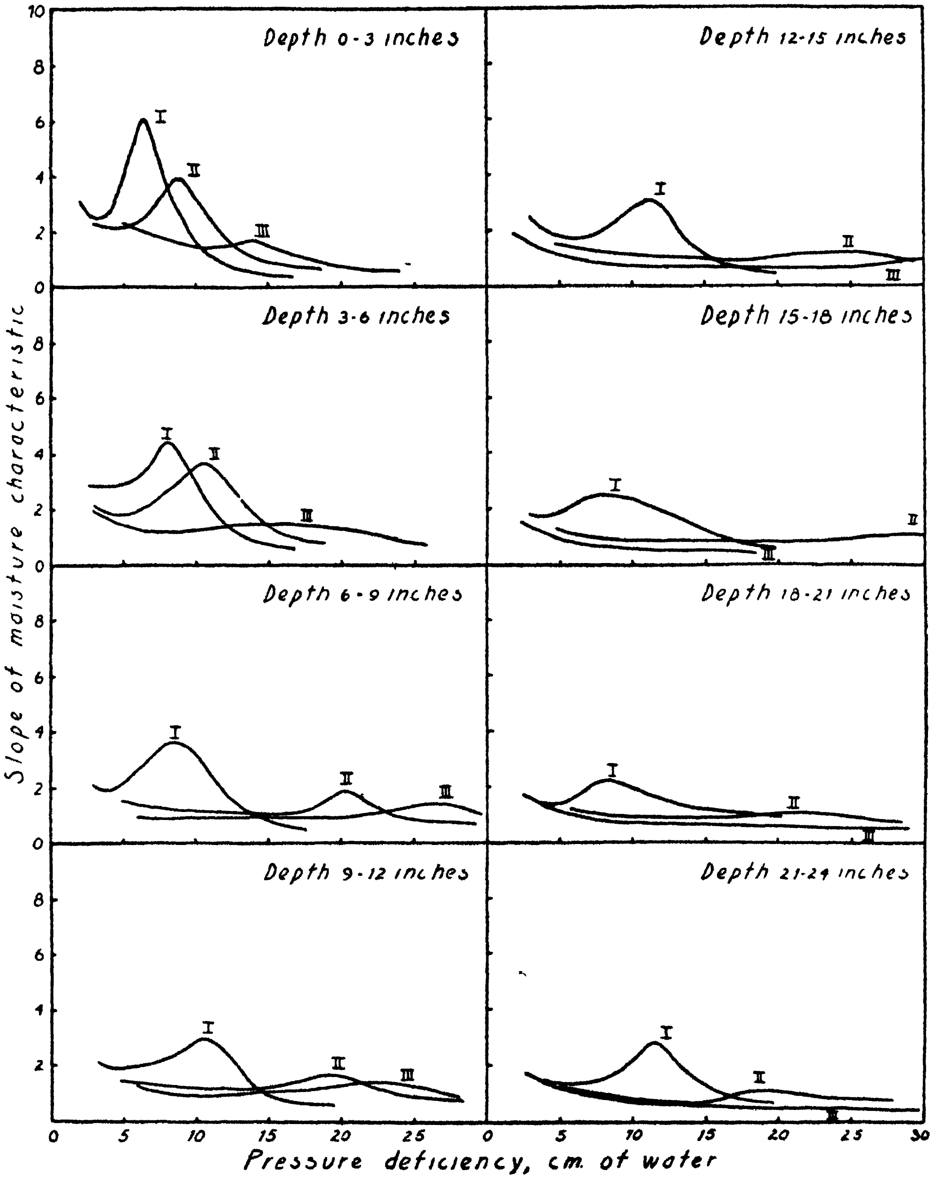

FIG. 3. DIFFERENTIALS OF MOISTURE CHARACTERISTICS FOR LOWER LIAS CLAY AT VARIOUS DEPTHS, BEFORE AND AFTER ARTIFICIAL WEATHERING

Curves I—III, as in figure 1

trality, whereas the more stable Upper Lias, very similar in all other respects, is devoid of free calcium carbonate and is markedly acid. Whatever may be

the importance of calcium carbonate, other things being equal, it is clear that, as between different soils, there is some other factor of great importance to stability. This factor may be clay mineral type, but further discussion of this point is not yet possible; the matter is one for separate investigation.

Among minor points it may be noted that the Upper Lias surface soil shows apparent superstability to one cycle of weathering, the second curve having a more pronounced peak than the first. This soil, however, seemed quite distended with organic matter; the dry crumbs floated in the Büchner funnel when water was first added, and even when wet the crumbs were extremely resistant to settling and packing. In these conditions experimental errors tend to be larger than usual. The only safe conclusion to be drawn is that the soil is remarkably stable. Only marked differences and modifications of characteristics due to weathering can profitably be discussed, the more so because pore-space modification is very sensitive to crumb disintegration. In many instances, when all trace of a defined pore group, as indicated by the differential of the moisture characteristic, is removed by weathering, as in the Middle Lias, 12–15-inch depth, the crumb structure is still very obvious to the eye; whereas a modification of a stable crumb producing a marked modification of characteristic, as in the Lower Lias 0–3-inch depth after one cycle of weathering, is barely perceptible to the eye. In this sensitivity, of course, lies the advantage of the method.

One curious feature of the curves for the Middle Lias may be noted. The surface soil shows signs of weathering into two distinct groups of pores, one being of the original pore size whereas the other suffers modification in the usual way. It would appear that there are two groups of crumbs, one of which is more stable than the other. From information at present available one can only speculate as to the cause of this phenomenon.

DISCUSSION, WITH PARTICULAR REFERENCE TO MOLE DRAINING

Before mole draining is considered more particularly, it is well to observe once more the overwhelming stabilizing effect of humus in the topsoil. This is recognized in a general way; the excellent tilth and superior drainage properties of newly broken heavy grassland are well known. The point which emerges here is that nothing else seems to be comparable in importance to humus, and therefore to resuscitate worn-out arable clay land and to render it once more capable of producing a good tilth there is probably no alternative to the long fallow period, which alone can economically and adequately restore the humus content.

In connection with mole draining, the Middle Lias will not be further discussed, since the sample examined was a light to medium loam obviously unsuited to the operation. The stability of the Upper and Lower Lias is considerable at all depths examined, but in mole draining we are most interested in the stability at depths of 18 to 24 inches, at which, for good reasons, the mole channels are commonly drawn; though main moles drawn by steam

tackle or its modern Diesel equivalent are occasionally somewhat deeper. It must first be observed that the results given by the stability curves cannot be applied directly to forecast the number of seasons the drains are likely to last, on the basis of one wetting and drying cycle per annum. The artificial weathering cycle of the experiments has the extreme range air-dryness to saturation, which is certainly not the case in nature at the depth of the mole channel. For example, in undisturbed Gault clay at a depth of 24 inches it is known that the typical variation of moisture content is from about 27 per cent in summer to about 32 per cent in winter, reckoned as percentage of dry weight (4), although the range is almost certainly wider at the walls of the mole channel itself. The change, moreover, is slow in the field, whereas the rapid change in the experiments is certain to have a greater disrupting effect. This was demonstrated quite simply by dividing a crumb fraction of a clay of low stability (Wadhurst clay from Kent, containing 61 per cent clay)

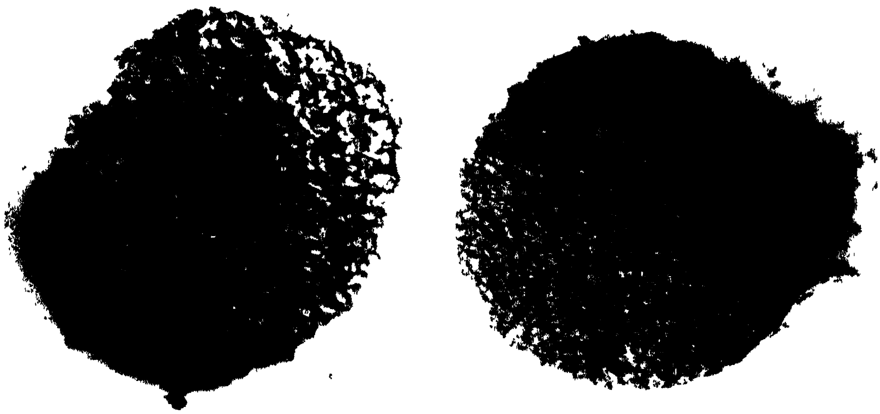

FIG. 4. DISINTEGRATION OF CRUMBS OF WADHURST CLAY PRODUCED BY SLOW WETTING (LEFT) AND BY RAPID WETTING (RIGHT)

into two portions, one of which was wetted quickly in the ordinary way, and the other, slowly by means of a wick dipped into water, the other end being embedded in the clay crumbs. In this latter way the crumbs were saturated in about 24 hours, and were then covered with distilled water and left to soak over a week end. As shown in figure 4, the slowly wetted crumbs were not visibly changed by the process, whereas the rapidly wetted sample was drastically modified. The experimental weathering cycle corresponds rather more closely to that experienced by surface soil in the field; at the surface there are many cycles in the course of the year, some of which approximate the range air-dryness to saturation. It is possible that by carefully controlling the weathering cycle in the laboratory to simulate that in the field we could roughly assess the probable life of the mole channel, barring accidents. Such possibilities are being investigated, but in the meantime it is necessary to proceed otherwise.

The stability curves are used here to compare the unknown soil with one of proved suitability for mole draining. One of the most reliable of these occurs on the Gault. In figure 5 are given the differentials of the moisture characteristics of a Gault profile from old grassland on the Cambridge Uni-

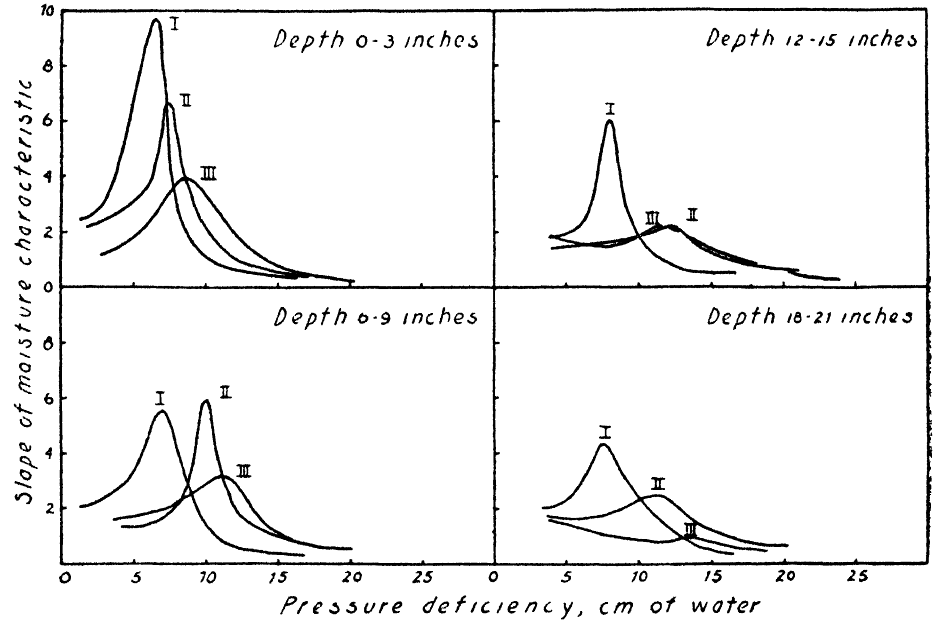

FIG. 5. DIFFERENTIALS OF MOISTURE CHARACTERISTICS FOR GAULT CLAY AT VARIOUS DEPTHS, BEFORE AND AFTER ARTIFICIAL WEATHERING
Curves I—III, as in figure 1

TABLE 2
Mechanical analyses of Gault profile

DEPTH	CLAY	SILT	FINE SAND	COARSE SAND	$CaCO_3$	ORGANIC MATTER	LOSS ON SOLUTION	H_2O*
inches	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
0– 3	42.00	14.75	8.50	6.71	3.53	10.52	4.60	12.71
6– 9	47.00	18.00	10.63	7.64	4.76	2.64	3.25	7.41
12–15	50.25	18.00	6.44	2.59	12.58	1.38	2.92	6.99
18–21	41.25	17.75	2.74	2.26	25.84	1.08	2.60	8.04

* Content of air-dry soil.

versity Farm, mole drains in which have been under observation for a number of years and are known to have reasonably long life. The mechanical analyses of this profile are given in table 2. The profile was sampled in alternate 3-inch layers, the routine work being thereby much reduced with only negligible disadvantage, the stability changing very regularly through the profile.

It will be seen that the Upper Lias, except at the 21–24-inch depth, as already mentioned, and the Lower Lias, to a less extent, are comparable in stability to the Gault. It is therefore reasonable to suppose that both formations give soils suitable for mole draining. One cannot generalize about a whole geological formation on the basis of one profile examination, but in a case such as that of the Upper Lias described above, where the soil at depth is decidedly less stable than that nearer the surface, there is a danger that deep moled mains might lie in a horizon of low stability with consequent risk to the whole system. Tiled mains, always desirable, might in such a case be imperative.

The stability of the two Lias clays as revealed by their moisture characteristics is of such an order that one is justified in recommending mole draining without hesitation. The question remains: what is the value of the method in border-line cases; what degree of instability is associated with distinct possibility of mole drain failure? An answer to this question must wait until we have examined sufficient cases of failure of mole drains in soil judged suitable for the operation. It is not likely that a definite answer is to be obtained easily, since it is generally possible to find, as a reason for failure, a plausible alternative to faulty judgment of soil, such as unpropitious weather during or immediately following draining operations. But a start has been made on these lines, and three cases of drain failure have already been examined. It was found that the order of decreasing stability according to the laboratory tests was also the order of seriousness of closure of the mole channels, but in each case it is possible to maintain that drain failure was due to some cause other than unsuitability of soil. One of these failures occurred on Gault, and a crumb fraction separated from soil near a mole channel showed only a trace of a definite pore group even in the initial characteristic; after one cycle of weathering all trace of this group disappeared. These remarks apply also to a failure in Boulder clay. Both failures occurred in different parts of the same large field, which was drained at an unsuitable time when the ground was hard after the summer drying period, although evidently not so hard at depth as to render the operation impossible. It is therefore arguable that unsuitable condition at the time of moling was the true cause of failure. In the third case, in Oxford clay, stability at the moling depth proved to be comparable with that of the Upper Lias at 18–21 inches, as shown in figure 1. General closure of the channels was not so serious as in the other two cases, and failure was almost certainly due to sand pockets, some of which could be seen exposed in the outfall trench. It is possible that better evidence of the value of the test in doubtful cases will be forthcoming in the next mole draining season. Some of the clay soils examined so far, although possessing high clay fraction contents of the order of 60 per cent, nevertheless show very poor stability. If in the present emergency an attempt to mole drain these soils is considered a justifiable speculation, we should have direct confirmation or contradiction of the laboratory evidence.

Discussion of this method of investigating stability cannot be left without

mention of an interesting type of instability exhibited by a sample of London clay. This sample came from an unknown depth out of a bomb crater, and showed evidence of being parent material rather than subsoil. This point is emphasized because it is not desired that any remarks made about it here should be interpreted as condemning this clay for mole draining. The mechanical analysis, on a percentage basis, is as follows: clay, 54; silt, 17.75; fine sand, 22.46; coarse sand, 1.05; $CaCO_3$, 0.03; organic matter, 0.17; loss on solution, 1.02; H_2O in air-dry soil, 6.82. The differentials of the moisture characteristics are given in figure 6b. All three curves are for the first wetting after the separation of the crumb fraction, but the period of soaking before

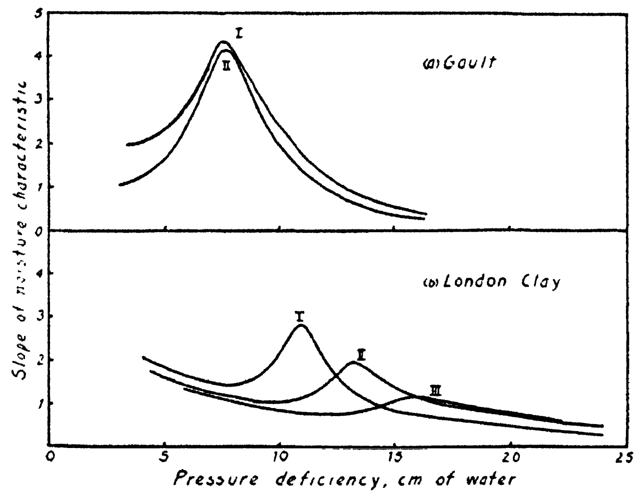

FIG. 6. INITIAL MOISTURE CHARACTERISTIC DIFFERENTIALS FOR 1–2-MM. CRUMB FRACTIONS OF (a) GAULT AND (b) LONDON CLAY

(a) Curve I, after normal 24-hour preliminary soaking. Curve II, after 120-hour preliminary soaking. (b) Curve I, after normal 24-hour preliminary soaking. Curve II, after 48-hour preliminary soaking. Curve III, after 96-hour preliminary soaking. These curves show the stability of the Gault and the instability of the London clay when left undisturbed in water.

the characteristic was taken varied from the usual 24 hours for sample I to 48 hours for sample II and about 96 hours for sample III. It will be seen that this clay continues to disintegrate progressively over a period of many hours or even days while undisturbed under water, a result which is rather surprising. The greatest stresses are, as we have seen, set up during the initial rapid and uneven wetting, and one would imagine that such disintegration as occurs would be complete within a few hours of completion of wetting, some few hours probably being required for the disintegration products to settle into their final positions. That such is ordinarily the case is shown in figure 6a, in the two curves for the Gault subsoil, from a depth of 18–21 inches, once wetted. Curve I is reproduced from figure 5 and is for the

usual 24-hour preliminary soaking; curve II was obtained after 120 hours' soaking. It will be seen that the two curves are almost indistinguishable, the difference being comparable to that between reproduced curves for identical conditions. The same reproducibility of curves after widely different soaking periods was found in Gault topsoil after one cycle of weathering, and would doubtless have been found in every case in Gault had the labor been deemed warranted. It need hardly be mentioned that instability of the type shown by this sample of London clay would, if found in subsoil at moling depth, render mole draining a very doubtful speculation, since such soil is not water-stable and deterioration of the channels is likely to occur not only in the normal course of seasonal wetting and drying but also progressively during the drainage season itself.

Finally attention must be drawn to the possibility that the stability requirements of land for mole draining may apply to some extent to subsoiling, particularly to the more violent type of subsoiling such as gyrotilling. Such an operation produces a large total volume of interclod cavities into which water may percolate and possibly collect. If the clods are unstable they will break down into a sludge, particularly if attention is not paid to drainage before subsoiling. The resulting "porridge" may be worse than the initial state.

SUMMARY

The method of assessing soil stability by means of moisture characteristics taken before and after artificial weathering is applied to Upper, Middle, and Lower Lias clays. The results are discussed with particular reference to mole drainage, and it is shown that the Upper and Lower Lias are almost as stable as a soil on Gault, which is known to be suitable mole-draining land. Some known drain failures are discussed, but the amount of evidence yet collected is insufficient to allow us safely to interpret stability curves in border-line cases. A deep sample of London clay is shown to behave peculiarly in that it withstands the stresses of rapid wetting from the air-dry state and then disintegrates progressively over a period of days while undisturbed in the saturated state. Finally it is suggested that the subsoiling of unstable clay soils requires as careful consideration as does mole draining.

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METHODS OF OBSERVING SOIL FLORA AND FAUNA ASSOCIATED WITH ROOTS[1]

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This paper describes a method of observing active associations of organisms with growing roots at magnifications up to 900 diameters, and suggests modified procedures that minimize the disturbance and loss of the associated organisms when roots are removed from soil and processed for examination. Developed for use in studies of root pathology with particular reference to root-infesting nematodes, these methods appear to have a broader application in the study of the rhizosphere, where they may supplement advantageously the well-known plate culture and contact slide methods. The chief results of the nematode investigations are being published elsewhere, but a few observations on the rhizosphere are reported here.

OBSERVING THE ACTIVE RHIZOSPHERE

To enable examination of roots in place, at low magnification, the root observation boxes described by Dean (2) are excellent. For more detailed observation and for greater convenience where small plants are being investigated, the miniature observation box described by Linford (5) presents distinct advantages: this box is of such size that it may be placed on the stage of a microscope, and the optical quality of the double-width microscope slides employed as sides of the boxes allows effective observation at higher magnifications, including not only the dissecting binocular but the lower magnifications of the compound microscope as well. A 20× achromatic objective has sufficient free working distance to focus through the glass and still permit illumination with incident light, but the definition thus obtained is inferior. Vastly improved results have now been obtained by using a coverslip as the glass against which both roots and soil lie.

For observations of short duration employing young seedlings from small seeds, a suitable observation chamber has been constructed by cementing a circular coverslip to a large Van Tiegam cell ring so that the coverslip constitutes the bottom of a miniature dish. Sprouting seeds are placed in the dish near one side, covered with soil or other appropriate medium, and watered. The dish is then incubated in a moist chamber tipped at such an angle that roots grow across the bottom of the dish. Parasites or other organisms to be

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observed may be added if desired. For observation, the dish is inverted on the stage of the microscope.

For observations over longer periods or involving the roots of somewhat larger plants, miniature root observation boxes of the type referred to above have been modified by cementing a coverslip over an opening cut in a side of the box. To permit use of a 24- by 50-mm. coverslip, a rectangular opening 16 by 43 mm. was cut in a central position in the 2- by 3-inch glass slide by means of a stone-cutter's sand blast. The coverslip was then cemented over this opening with waterproof lacquer or dilute balsam and, after thorough drying, the slide was fitted into the observation box. To receive 45- by 60-mm. coverslips, sheet brass was cut to 2 by 3 inches with a rectangular opening 1½ by 2 inches. In cementing the coverslip over this frame, care was taken to coat all brass surfaces with lacquer to prevent contact of roots or soil with the metal.

In the selection of microscopic objectives for examination of such cultures with incident light, ample free working distance is more important than the highest degree of correction. Apochromatic objectives 10× and below are suitable, but at 20× the achromatic type is superior because its greater free working distance allows better illumination. These dry lenses permit observation of objects in air pockets under the coverslip, but the more powerful immersion lenses resolve sharply only objects that are immersed in films of water beneath the coverslip. In the writer's experience, dry lenses of higher power are not adaptable. The most generally useful lens thus far employed is an achromatic, water-immersion objective, 40×, 0.75 N.A., with the great free working distance of 1.9 mm. A 90× apochromatic oil immersion objective, N.A. 1.30, free working distance 0.14 mm., has also been used successfully with 10× oculars, but adequate illumination for binocular observation is achieved with some difficulty.

Illumination is provided by a large microscope lamp fitted with a 100-watt bulb, adjustable condensers, and a water cell for cooling the light. The beam of light is directed downward on the object at a low angle (an especially low angle is required with the oil immersion objective), and is brought to a sharp focus with a strong plano-convex lens or a spherical flask of water. A large

PLATE 1

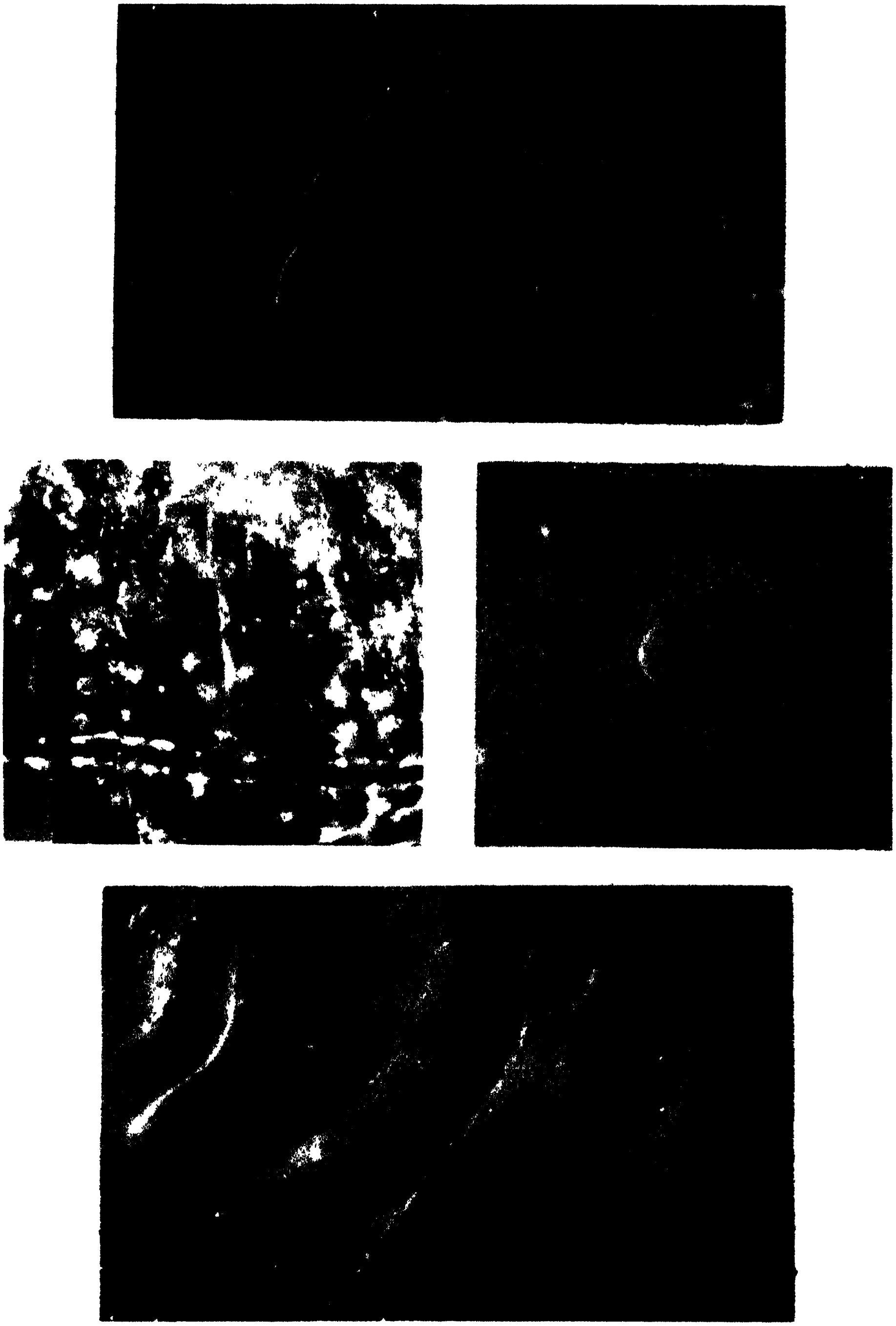
LIVING MICROORGANISMS ASSOCIATED WITH ROOTS, PHOTOGRAPHED IN OBSERVATION BOXES WITH INCIDENT LIGHT

FIG. 1. Coarse, septate mycelium growing on the surface of a young maize root, with hyphae curved around two very young root hairs; also bacteria, associated especially with root hair at right. 890 ×

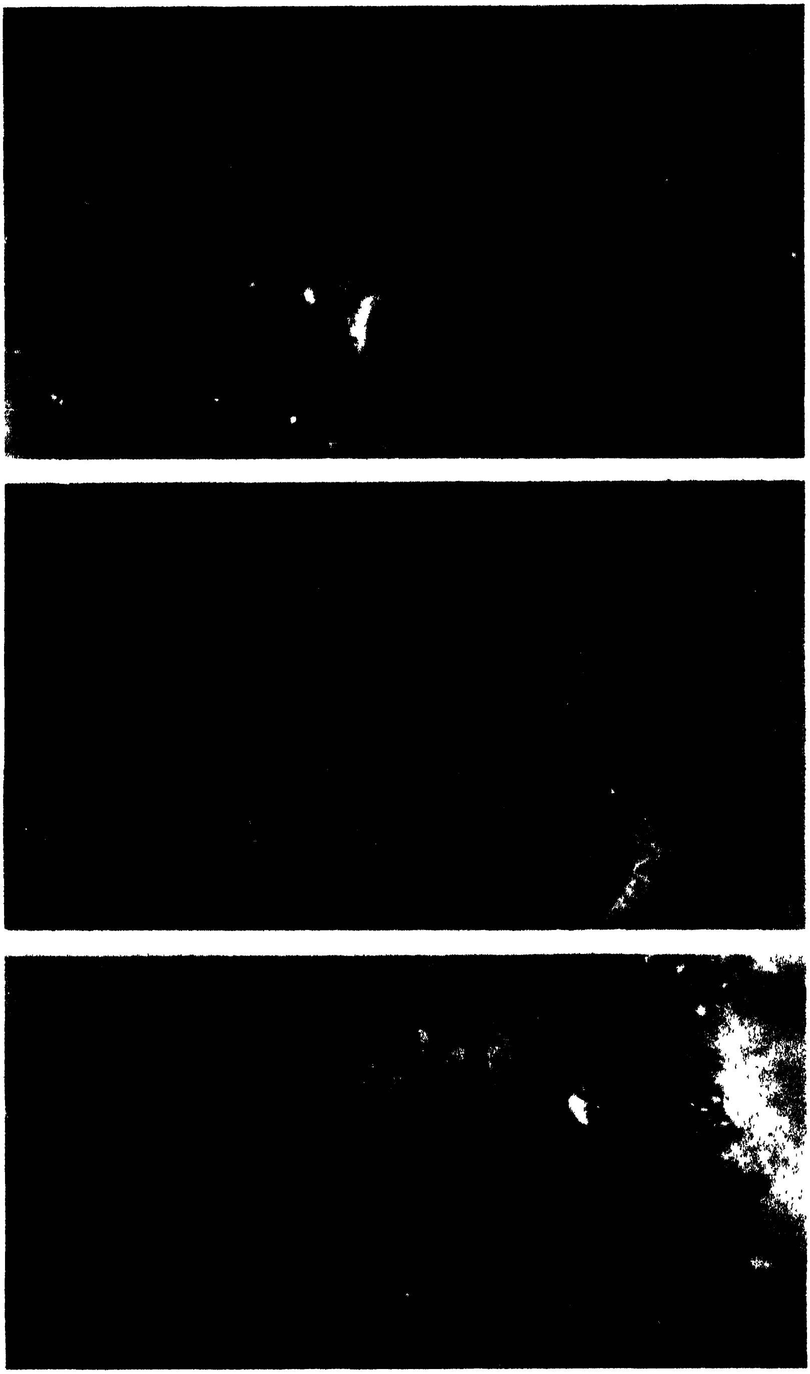
FIG. 2. Hyphae and conidia of an undetermined fungus in an air pocket at the side of a pineapple root tip. 400 ×

FIG. 3. Optical transverse section of a massive bacterial colony completely encircling a cowpea root hair. This colony extended down to the root surface and also up above the plane of focus. The root hair was still alive. 890 ×

FIG. 4. Bacterial colonies at bases of cowpea root hairs in region about 48 hours old. 760 ×



FIGS. 1-4



FIGS. 5-7

immersion drop focuses the light still further. One lamp provides ample illumination for use with the 40× objective and a pair of 15× or 20× oculars, but two such lamps set at opposite sides of the microscope facilitate obtaining the most effective angle of illumination. A striking peculiarity of these conditions of observation is that even a slight difference in orientation of the object with respect to the source of light may make a vast difference in the visibility and definition of even relatively large objects. Because of this a revolving stage is almost a necessity, and from other considerations a mechanical stage fitted to carry large objects is desirable.

This method serves to bring under direct observation certain details not readily studied otherwise, but it has some sharp limitations. The small ring chambers are useful only when very small seedlings are to be studied for but a few days. The writer has used them chiefly in studies of nematodes before and during penetration into roots. Even the miniature observation boxes are suitable only for small plants and require exacting attention. Because of the small soil volume, moisture content is reduced rapidly by a transpiring plant, and it is difficult, with daily care, to avoid alternating extremes of soil moisture. Photomicrographs are made in the ordinary way but, as might be expected with the unstained objects and the limitations of illumination, contrast is characteristically low even after very full development of the negatives. Specimen results appear in figures 1 to 7, and some observations are recorded in a following section

At any desired time the glass side of the box may be removed and stained as though it were a "contact slide." The writer has found Conn's rose bengal stain suitable when applied for 10 minutes as used by Starkey (7). By marking points of particular interest before removing the slide from the box, one can make comparative observations of live and stained material. Roots exposed by removing the glass may be examined with a dissecting binocular and selected parts removed for culturing or for further examination

EXAMINING ROOTS REMOVED FROM SOIL

Mycologists and pathologists have made extensive use of lactophenol containing an appropriate stain, since Davis (1) directed attention to its usefulness for the rapid preparation of certain plant and animal materials for microscopic examination. Goodey (3) adapted this technique to the demonstration of

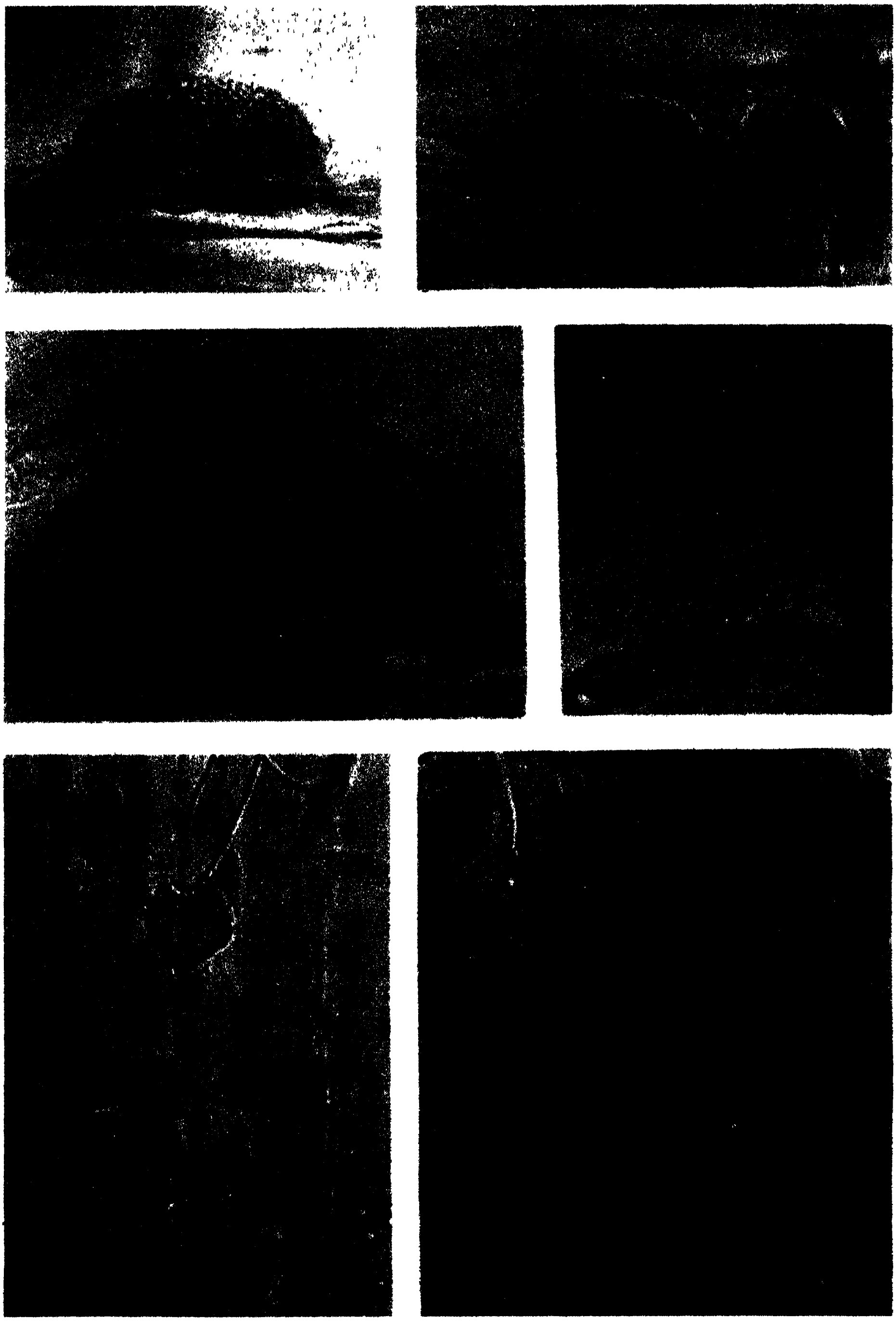
PLATE 2

LIVING MICROORGANISMS ON ROOTS, PHOTOGRAPHED IN OBSERVATION BOXES WITH INCIDENT LIGHT

FIG. 5. Scattered bacterial rods on surface of cowpea root in region less than 24 hours old where root hairs were just beginning to develop More cells of similar shape were actively motile and do not show in this 2-second exposure. 760 ×

FIG. 6 Great numbers of irregularly disposed bacterial rods on surface of cowpea root in region 30 hours old. Some were motile at the margins of this diffuse colony. 890 ×

FIG. 7 Surface of maize root, showing two or more bacterial colony types (lower part), and a protozoan brought to rest by chilling of the culture (upper center). 760 ×



FIGS. 8–13

nematodes within roots and, more recently, McBeth, Taylor, and Smith (6) have proposed further modifications to increase its usefulness where a census of nematodes within roots is to be taken. The procedures proposed here are useful when interest centers in microorganisms associated with the surface of nonwoody rootlets.

The first step is to plunge roots into a volatile fixing fluid immediately after their removal from soil, with no prior washing. A formalin-acetic-alcohol solution is allowed to act for one or two hours warm or longer cold. The fixed roots are lifted to open dishes of clear lactophenol and heated in an oven at about 100°C. until they have stopped clearing. Boiling speeds clearing but possibly disturbs the root surface unnecessarily. Sufficient acid fuchsin solution is then added to color the medium a deep pink and is allowed to act only a few minutes before the roots are transferred to clear lactophenol for examination. Too long contact with the stain results in deep penetration, which is undesirable where maximum transparency is desired for observation of the root surface. For a study of organisms within the root, a weaker stain solution and longer exposure are better.

At this stage the amount of soil adhering to the root varies with the type of soil and the abundance of root hairs. Some roots may be almost completely encased in soil, but usually at least the youngest parts are nearly clean and can best be removed for examination at this stage. Many significant observations can be made where considerable soil is present. Pieces of root with too much adherent soil may, in some instances, be cleaned sufficiently by loosening clumps of soil with needles while the root is immersed in lactophenol. In extreme cases it becomes necessary to wash gently in water, return the root to lactophenol, and, if needed, add more stain. Roots that come from the soil almost clean can be plunged directly into lactophenol, but prior fixation preserves the root protoplasts in better condition, a factor of interest in many

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PLATE 3

MICROORGANISMS PHOTOGRAPHED ON ROOTS PROCESSED WITH FORMALIN-ACETIC-ALCOHOL AND LACTOPHENOL WITH ACID FUCHSIN

FIG. 8. Massive bacterial colony seen in profile on root of lettuce seedling, showing columnar arrangement of cells near the base of the colony. 890 ×

FIG. 9. Similar to figure 8, but showing a distinctly compound colony and a smaller simple colony on maize root. 690 ×

FIG. 10. Optical section of a massive bacterial colony completely encircling the base of a lettuce root hair. Observe the root hair nucleus near the right wall in the upper half of the colony. In a different focal plane the columnar arrangement of cells resembled that in figure 8. Compare with figure 3. 890 ×

FIG. 11. Bacterial colonies distributed over young maize root. The small dark area between the root hair and the largest colony is a colony of rods too small to be resolved in this photograph. 690 ×

FIG. 12. Relatively large spherical to ovoid cells of undetermined nature clustered on pineapple root hairs. Bacterial rods also were present in these clusters. 690 ×

FIG. 13. *Penicillium* sp. growing from dead root hairs on young root of pineapple. Observe that conidia remained attached during processing of the root. 380 ×

studies of associated organisms. The writer has made no attempt to prepare permanent mounts, but the methods of Goodey (3) or McBeth et al. (6) should prove suitable.

With this procedure (figs. 8 to 13) the writer has retained on the root surface and among root hairs, not only bacteria, actinomycetes, and various fungi, but also protozoa and nematodes, both free-living and parasitic. Bacterial colonies of types that disintegrate in water have been retained, and delicate hyphae have been more numerous and better preserved than on roots washed before fixation. Even with the most cautious handling, certain organisms drop away from the roots, and examination of the soil and debris in the bottom of the staining dish may reveal the presence of brightly colored nematodes and other animal forms.

SPECIMEN OBSERVATIONS

Using the observation box technique and root processing as here described with seedlings of maize, lettuce, and cowpea, and with pineapple plants grown from diminutive slips of a proliferating mutant, the writer has observed living associations about young roots chiefly in a very fine but granular soil from one pineapple field. More limited studies with other Hawaiian soils have given somewhat similar results. The observations reported here both illustrate the usefulness of the method and help to describe the rhizosphere.

Remote from roots, microorganisms were generally difficult to detect and appeared to occur only sparsely. There were coarse hyphae of an undetermined fungus distributed widely but sparsely through the soil, and small colonies of a more delicate fungus developed on scattered bits of organic matter. Bacteria were not recognized with certainty, although their presence was established when the glass sides of certain boxes were removed and stained with rose bengal. Scattering bacterial growth was then seen to be widely distributed, with different cell types in sparse and usually indefinite colonies. Protozoa and nematodes were nowhere abundant remote from roots.

On and near the root surface, however, this method revealed much that was missed when the contact slide method was employed. The soil in question contained many *Paratylenchus* sp., small nematodes that gathered around the roots to feed with their stylets inserted into epidermal cells and root hairs. Initial stages of the feeding and penetration of other root-infesting nematodes were also studied. Details of those observations will be reported elsewhere. Microphagous nematodes, including rhabditids and cephalobs, were active at various points along the roots, especially in the younger zones and about the root caps of some roots more than others, apparently feeding on bacteria that were abundant there. Protozoa also became conspicuous, including small flagellates and large infusoria (fig. 7), moving about in the thin films of water on the epidermis and root hairs.

Fungi on the roots were of varied types. The root hair parasite *Rhizidiocystis ananasi* Sideris was conspicuous on, in, and between root hairs of pine-

apple only. Over the surface of pineapple, cowpea, and maize roots, and penetrating at least the epidermal cells at some points where no pronounced disintegration of tissues followed, were certain coarse, septate, sparsely branched hyphae (fig. 1). Various other fungi were seen, including a Penicillium and an undetermined imperfect that grew from a few roots into air pockets and sporulated there (figs. 2, 13). Both at root tips and occasionally on and among root hairs, the delicate, tangled growth of an actinomycete was seen, especially when the soil was rather dry, and at times very delicate threads, probably of such an organism, were distinguished in the water film between root and glass.

The bacteria (figs. 3 to 11) were especially interesting and surprising because of their abundance on very young roots and of the relatively large and distinct colonies that some of them formed. Motile bacteria (figs. 5, 6), often in enormous numbers, moved actively in the water films between root and glass and along root hairs, and often were abundant even around the root cap. Colony formers began to appear in the elongating zone, the colonies enlarging and new ones forming as the root matured. Judging by colony type and cell size and shape, several species were present (figs. 7, 11). One type, not illustrated, was relatively thin, with large rods widely and rather uniformly spaced, as if separated by gum. Massive colonies, apparently firm and with cells closely packed (figs. 8, 9, 10), were especially conspicuous, and sometimes formed collars surrounding root hairs either near the root or farther out. In at least the younger of such root hairs, the protoplast was streaming actively and apparently normally (figs. 3, 10). Such colonies were found on roots growing through air spaces, in compact soil, and where the root was tightly pressed against the glass. On cowpea, lettuce, and corn they were relatively more abundant than on pineapple, but even here they were too conspicuous to be missed with rapid examination at 400 diameters or greater magnification. In the root zones studied there was no notable grouping of bacteria around the sloughed off root cap cells.

These observations indicate that the early concentration of microorganisms in the rhizosphere is not dependent upon the destruction and utilization of senescent and dead root cap cells, root hairs, and cortical tissues. Most likely many of the associates of older roots are there as scavengers. The bacteria that congregate abundantly around meristematic to young but mature root zones, however, apparently either are utilizing nutrients that diffuse out of the active root cells or are otherwise benefiting from a local alteration of the soil environment under the influence of the root. Protozoa and microphagous nematodes are either attracted to the zones of great bacterial activity or multiply more rapidly there where food is abundant, or both. The plant-parasitic nematodes, as shown earlier by the writer (4), are definitely attracted to roots, different species being selectively attracted to different root zones. Fungi, so far as here observed in association with young roots, probably are chiefly parasitic.

Different conclusions would have been reached if the stained slides alone

had been observed. Such slides rarely retained nematodes even when these were known to be abundant in the rhizosphere, and, as reported by Starkey (7), protozoa could not be recognized as such from the deeply stained remains on the slides. Certain fungi present in abundance on roots appeared only sparsely on the slides, and conidia of Penicillium were so collapsed and distorted as to be unrecognizable from the slides alone.

The stained slides were superior for differentiating bacterial cell types, but they gave a very incomplete record of bacteria associated with young roots. Virtually all the larger, compact colonies were removed with the root, as were also great numbers of the bacteria swimming in films of water on the epidermis and root hairs (which are lost also when a root is processed), and there is reason to suspect that some of the apparent colonies on stained slides result from the drying of films of motile cells around larger particles adhering to the glass.

SUMMARY

Direct observations, at magnifications up to 900 diameters, of organisms associated with roots growing in soil are possible where roots are grown in contact with a glass coverslip. Small seedlings may be grown a few days in observation chambers made by cementing coverslips to glass rings. These chambers are inverted on the microscope stage for examination. Observations of roots of larger plants and over longer periods are possible where coverslips are cemented over openings in the sides of miniature root-observation boxes of the type described earlier by the writer. Observation is with cooled incident light. This method enables observation and photographic recording of living bacteria, actinomycetes, fungi, protozoa, and nematodes on and about the root. The glass sides of the observation boxes may be stained as contact slides.

When processing roots in lactophenol with an appropriate stain, where interest centers in organisms on the root surface, it is recommended that unwashed roots be fixed in formalin-acetic-alcohol and that they be processed in lactophenol without washing or with the least washing that will permit observation of the necessary details. In this way, many microorganisms and nematodes that are lost by a preliminary wash are retained among the root hairs or on the root surface. A brief period of staining after the roots are clear brings out surface details while retaining transparency.

The use of these methods with roots of four plant species has shown that varied bacteria become numerous in intimate association with very young roots, down to the apical meristem, and that protozoa and microphagous nematodes congregate and multiply here. The view that microbial activity in the rhizosphere is related chiefly to destruction of senescent cells is shown to be inadequate.

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THE COMPARATIVE PHYSICAL CONSTITUTION OF WATER-STABLE GRANULES AND OF THE ORIGINATING SOIL[1]

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Granules are probably produced in soils partly by the disintegration of the more massive physical units or clods and partly by accretion. In either case, organic and inorganic colloids play a major role. The mechanism by which granulation, or aggregation, is brought about is partly known but certainly not fully understood. It is being actively investigated at this time by several workers.

Inasmuch as there is no direct positive evidence regarding the distribution of the finer fraction of the soil within the various aggregates of the coarser dimensions, it seems desirable that this information be obtained. It is of practical significance in considering the loss of soil by erosion, in that were all the highly important nutrient-containing colloid and clay fraction to be cemented into coarser stable aggregates, permeability would be greatly enhanced and the loss of the most easily transportable soil fraction would be retarded because it was a principal constituent of a heavier, less movable granule.

Baver and Harper (2) have shown that failure of certain desert soils to form aggregates larger than 0.05 mm. is associated with the low clay and organic matter content of such soils. Baver (3) has observed a close correlation between both the percentage of clay and organic matter and the aggregation of 77 widely different soil types.

Sideri (11, 12) and Myers (7) attempt by their studies on aggregation with the use of selected organic and inorganic aggregate constituents to contribute explanations regarding the chemical and physical mechanisms involved in the phenomenon of structure formation. Peele (9) and Martin and Waksman (5) have demonstrated a relationship between microbial activity and soil aggrega-

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tion. Metzger and Hide (6) working with Derby silt loam of Kansas found that organic matter content increased as the size of the aggregate increased and that the ultimate mechanical composition of aggregates of different sizes was similar. Later, Hide and Metzger (4) reported that aggregate analysis fractions of differently treated experimental soils differed in their physical make-up. The well-aggregated soil was characterized by granules high in clay and sand, whereas those from the poorly aggregated soil possessed a high silt content. Base-exchange capacity of each aggregate size fraction, as might be expected, varied with clay content.

The purpose of the present investigation was to determine whether the aggregates in a given soil are mechanically like the whole soil or whether they are composed of a greater proportion of fine material, including organic matter. In case the aggregates have a mechanical composition identical with that of the whole soil, we might assume that the aggregates in that soil were formed contemporaneously with the development of the specific horizon. This may have been accomplished either through the degradation or disintegration of more massive structural units or by the cementing of smaller inorganic and organic particles into the natural soil crumbs. If the aggregates are composed of a greater percentage of fine particles than that found in the whole soil, one might infer that they were formed by accretion following dispersion of the clay fraction. By this process the clay and finer colloids, dispersed from other soil particles, formed into concretionary units containing a smaller proportion of the sand and gravel sized particles than the whole soil.

MATERIAL AND METHODS

To examine this question several soils were obtained which were derived from parent material of widely different geological origin in Pennsylvania. In each case the A_1 horizon of forested areas was chosen. Closely adjacent cultivated areas were studied in a few cases for comparison.

The Atterburg scale of class size limits was adopted in this study. The coarse sand element of 2–0.2 mm. was divided into two subfractions, the limits of which are 2–1 mm. and 1–0.2 mm. A complete mechanical analysis of each whole soil was made by a modification of the pipette method (8) as described elsewhere (1). Aggregates for further study were obtained in the following manner: A large sample of the original unsieved soil was slaked in distilled water for 24 hours and, after the loose undecomposed organic debris in the supernatant liquid was floated off, the residue was transferred to a nest of sieves having aperture diameters of 0.2, 1, and 2 mm. Standard screens of 70, 18, and 10 meshes per linear inch were used to effect this mechanical separation. A gentle stream of water was then applied to the material on the screens to wash off any loosely adhering finer particles. The contents of each screen were then subjected to further dispersive forces (14) by plunging into a water bath at the rate of 20 plunges per minute for 5 minutes to effect a more complete segregation of the water-stable aggregates and primary particles of each

size class. After drying at 105°, the aggregate accumulation was spread on a sheet of glazed paper and the true granules were separated from the discrete particles by means of a hand lens, spatula, and camel's-hair brush. At least 25 gm. of "hand-picked" aggregates of the 1–2 mm. and > 2 mm. size class were obtained in this way. It was not feasible to separate granules from the discrete particles in the 0.2–1 mm. size; therefore, this separate includes both primary and secondary particles.

TABLE 1

Condensed description of the soils studied

SERIES AND TYPE	PARENT MATERIAL	FORMATION OF MATERIAL	DRAINAGE	SAMPLING SITE
Ravina* loam	Calcareous shales and sandstones	Glacial (ground moraine)	Fair	Forest
Canfield clay	Calcareous shales and sandstones	Glacial (ground moraine)	Poor	Forest
Erie clay	Calcareous shales	Glacial (ground moraine)	Fair to poor	Forest
Lackawanna sandy loam	Red shales and sandstones	Glacial till and residual material	Good	Forest
Ashe loam	Rhyolite	Residual (igneous extrusive)	Good	Forest
Montalto clay loam	Diabase	Residual (igneous extrusive)	Good	Forest
Hagerstown clay loam	Limestone	Residual	Good	Forest and cultivated
Penn clay loam	Triassic shales and sandstones	Residual	Fair to good	Forest and cultivated
Chester clay loam	Gneiss and schist	Residual (metamorphosed igneous)	Good	Forest and cultivated
Tioga loam	Acid glacial and Piedmont upland	Alluvial (first bottom)	Good	Forest
Chenango sandy loam	Acid glacial and Piedmont upland	Alluvial (terrace)	Good	Forest

* Originally correlated as Volusia.

The "hand-picked" aggregates and the whole 0.2–1 mm. fraction were analyzed mechanically in the same manner as the whole soil for comparison.

Organic matter was determined in both the whole soil and the aggregates by the chromic acid titration procedure of Schollenberger (10) as modified by Tiurin (13).

For purposes of correlation the stability index and the probable permeability of each soil considered were determined by the method of Alderfer and Merkle (1). Stability index is a physical measurement designed to indicate what percentage of a given soil exists in a structurally stable condition. Probable

TABLE 2

Mechanical analyses and organic matter contents of the water-stable aggregates compared with the whole soil from which they were derived

SIZE OF AGGREGATE	STABILITY INDEX	PROBABLE PERMEABILITY	ORGANIC CONTENT	CLAY <0.002 MM.	SILT 0.002–0.02 MM.	FINE SAND 0.02–0.2 MM.	COARSE SAND 0.2–1 MM.	COARSE SAND 1–2 MM.	GRAVEL >2 MM.
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Ravina—Forested									
>2 mm.			13.5	32.2	45.1	21.6	1.0	0	0.1
2–1 mm.			10.1	33.2	42.3	23.1	1.4	0	0
1–0.2 mm.			9.5	32.2	45.0	19.8	3.0	0	0
Whole soil	67.4	72.2	9.9	16.4	46.4	32.4	3.0		1.8
Canfield—Forested									
>2 mm.			3.1	21.2	41.1	27.6	4.5	1.0	4.6
2–1 mm.			2.7	17.8	41.3	33.4	5.8	1.7	0
1–0.2 mm.			2.7	17.4	40.6	27.7	14.3	0	0
Whole soil	46.1	54.3	2.3	20.9	34.0	30.2	10.0		4.9
Erie—Forested									
>2 mm.			6.4	39.9	42.3	16.5	1.0	.1	.2
2–1 mm.			7.2	40.6	43.0	15.6	.7	.1	0
1–0.2 mm.			7.1	38.9	43.4	15.3	2.4	0	0
Whole soil	74.8	75.4	8.0	33.9	42.9	21.2	1.7		.3
Lackawanna—Forested									
>2 mm.			1.7	24.2	37.0	27.6	4.3	.4	6.5
2–1 mm.			2.3	26.4	42.0	26.9	4.5	.2	0
1–0.2 mm.			2.4	23.9	37.2	25.1	13.8	0	0
Whole soil	47.7	70.4	1.7	17.1	34.8	25.4	12.4		10.3
Ashe—Forested									
>2 mm.			7.9	28.1	45.5	23.3	2.6	.2	.3
2–1 mm.			5.8	33.4	32.4	30.3	3.6	.3	0
1–0.2 mm.			5.3	22.4	51.0	23.0	3.6	0	0
Whole soil	59.8	66.2	3.2	19.8	45.9	25.7	3.7	.4	4.5
Montalto—Forested									
>2 mm.			2.1	24.8	44.1	26.3	2.6	.7	1.5
2–1 mm.			2.2	26.7	44.6	26.8	1.8	.1	0
1–0.2 mm.			2.3	26.8	43.2	25.4	4.6	0	0
Whole soil	71.4	74.3	2.1	24.3	45.8	27.0	2.7	.1	.1
Hagerstown—Forested									
>2 mm.			5.6	29.1	44.8	16.2	4.9	.5	4.5
2–1 mm.			4.6	28.7	46.1	18.4	6.0	.8	0
1–0.2 mm.			4.4	24.9	42.9	19.1	13.1	0	0
Whole soil	61.5	66.7	4.0	25.2	41.2	19.6	7.0	1.3	5.7
Hagerstown—Bluegrass sod									
>2 mm.			5.0	27.7	43.5	21.5	5.0	.1	2.2
2–1 mm.			4.9	25.0	45.1	23.2	5.7	1.0	0
1–0.2 mm.			4.2	23.1	44.3	18.6	14.0	0	0
Whole soil	69.6	54.1	4.4	20.7	50.6	17.6	7.3		3.8

TABLE 2—*Concluded*

SIZE OF AGGREGATE	STABILITY INDEX	PROBABLE PERMEABILITY	ORGANIC CONTENT	CLAY <0.002 MM.	SILT 0.002–0.02 MM.	FINE SAND 0.02–0.2 MM.	COARSE SAND 0.2–1 MM.	COARSE SAND 1–2 MM.	GRAVEL >2 MM.
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Hagerstown—Cultivated*									
>2 mm.			5.2	33.3	48.7	17.8	.2	0	0
2–1 mm.			3.9	24.1	59.8	15.3	.7	.1	0
1–0.2 mm.			3.3	24.8	55.9	17.6	1.7	0	0
Whole soil	66.6	20.3	2.5	24.7	55.9	18.8	.4	.1	.1
Penn—Forested									
>2 mm.			2.8	25.6	45.8	22.9	1.7	1.6	2.4
2–1 mm.			2.9	28.1	45.8	22.5	2.3	1.3	0
1–0.2 mm.			2.3	28.3	48.9	21.8	1.0	0	0
Whole soil	63.4	62.0	1.7	26.0	45.7	24.1	1.1	.3	2.8
Penn—Cultivated †									
>2 mm.			4.3	33.8	43.5	21.2	.9	.3	.3
2–1 mm.			3.9	26.6	45.8	25.4	2.0	.2	0
1–0.2 mm.			3.6	27.0	45.9	25.4	1.7	0	0
Whole soil	63.9	50.5	2.4	22.3	51.0	20.3	.7	.4	5.3
Chester—Forested									
>2 mm.			3.1	28.3	42.7	25.1	2.2	.4	1.3
2–1 mm.			3.3	28.6	41.6	25.7	3.4	.7	0
1–0.2 mm.			3.6	28.8	41.9	23.8	5.5	0	0
Whole soil	66.7	64.6	3.5	28.1	42.8	23.8	2.3	.2	2.8
Chester—Cultivated†									
>2 mm.			2.7	32.0	38.0	26.4	1.3	0	2.3
2–1 mm.			2.8	28.4	36.0	32.2	3.3	.1	0
1–0.2 mm.			2.3	27.4	38.3	28.1	6.2	0	0
Whole soil	58.1	46.8	2.0	25.5	40.0	27.1	2.5	.2	4.7
Tioga—Forested									
>2 mm.			3.6	12.4	16.7	48.3	22.0	.1	.5
2–1 mm.			3.8	14.7	19.2	44.8	21.0	.3	0
1–0.2 mm.			2.6	9.3	14.0	27.5	49.2	0	0
Whole soil	45.6	72.3	3.3	12.4	14.6	46.2	26.1	.3	.4
Chenango—Forested									
>2 mm.			3.6	19.4	43.6	36.5	.3	0	.2
2–1 mm.			3.3	20.8	39.0	39.7	.3	.2	0
1–0.2 mm.			3.3	19.6	35.6	44.0	.8	0	0
Whole soil	52.3	51.7	3.1	21.1	37.7	40.8	.4	0	0

* 49 years of continuous tobacco.

† Corn, oats, wheat, and clover rotation.

permeability designates that fraction of a given soil which consists of primary particles or water-stable granules capable of effecting optimum permeability relationships.

A condensed description of the soils chosen is given in table 1.

RESULTS AND DISCUSSION

Table 2 presents the complete physical analysis of the granules obtained from the various soils as well as that of the whole soil. The granules larger than 2 mm. and those between 2 and 1 mm., having been "hand-picked," are the ones to be referred to as such. The analysis of the unseparated 1–0.2 mm. fraction is included as supplementary information.

It appears that in the majority of cases organic matter has concentrated in the granules, as shown by the fact that the granules contain a higher percentage than the whole soil. The average increase in organic content of the aggregates as compared with that of the original soil is 24.12 per cent. It is also apparent that structural stability is closely related to organic content, the correlation coefficient between these two properties being +.66.

It is also true that in the majority of soils studied the clay content of the stable granules is higher than that of the whole soil, the average being 24.91 per cent more clay in the stable granules than in the whole soil. In a few cases there is very little difference between the clay content of the granules and that of the whole soil. Structural stability is closely related to the clay content, as reflected in a correlation coefficient of +.71. In those instances where the clay content of the aggregates differs significantly from that of the whole soil, there seems to be no single other fraction whose quantity is decreased in the granule by an amount corresponding to that percentage by which the clay has increased.

The probable permeability is influenced not only by the stability of the aggregates but also by their size. Furthermore, large particles are even more effective in producing permeability than are aggregates. The coefficient of correlation between total clay content and probable permeability for these soils was +.04, which is certainly not significant; however, the coefficient between organic content and probable permeability was +.55.

Close analysis of individual cases reveals some interesting opportunities for speculation.

The Ravina forested soil has an easily dispersed clay, not particularly rich in free iron oxide. It appears that in the genesis of this soil, the clay has dispersed and the soil particles have reaggregated into granules which are much higher in both clay and organic matter than the whole soil.

The Canfield forested soil, which is in the same catena as the Ravina but has poorer internal drainage, shows almost the same clay content in the larger stable aggregates as in the whole soil. The explanation appears to be that the poor internal drainage has resulted in swelling with subsequent clod formation upon drying and later disintegration (not dispersion) of the clods into smaller units of crumb size. Stability of these granules is undoubtedly enhanced by their increased organic content.

The Ashe and Montalto are both residual soils whose parent material is of igneous extrusive origin, commonly called "traprock." The Ashe is derived

from rhyolite and the Montalto from diabase. During the genesis of the Montalto soil, free iron oxides were produced from the ferromagnesium minerals in the decomposing diabase. These oxides aggregated along with the other clays into rather stable granules almost as soon as they were produced; hence, little dispersion took place within the profile, attributable in a large measure to the strong granulating effect of the iron, and consequently both granule and whole soil have the same clay content. The Ashe, on the other hand, being from rhyolite, is not notably rich in free iron oxides, and its clay is more easily dispersible. Both dispersion and reaggregation operate, therefore, within the profile and result in the large difference between the clay content of the granules and that of the whole soil. The stability index of the forested Montalto is high, 71.4, whereas that of the Ashe is only 59.8, affording further evidence of the above reasoning. It is obvious that both organic matter and clay combine to effect granule stability within the surface horizon of the Ashe.

The Tioga and Chenango are immaturely developed soils from geologically young parent material, the former a first bottom soil, and the latter a terrace soil along the Delaware River floodplain. These soil materials are too young for appreciable granulation to have occurred during profile development. Organic debris from the native forest is the chief granulating agency, as evidenced by the fact that it is higher in the coarser granules than in the whole soil. There is no significant difference in clay content between the granules and the whole soil.

The Chester is very old geologically, and during its long period of residual formation free hydrated iron oxides have been liberated from the igneous rocks. The Chester profile is well oxidized throughout. As with the Montalto, the clays were probably aggregated as fast as produced; hence, in the forested soil we find no significant positive difference between the clay or organic content of the granules and that of the whole soil. The cultivated Chester, on the other hand, shows a much higher clay content, in addition to an increased organic content, in the granule than in the whole soil. This is assumed to indicate that tillage operations and the exposure of the surface to rains have dispersed the natural granules, which have then reaggregated into new and different ones higher in these two physical constituents. The stability index and the probable permeability of the natural forested Chester is 66.7 and 64.6 as compared with 58.1 and 46.8 for the cultivated area.

The Penn soil, which is developed residually from Triassic formations, is relatively young geologically. The forested sample shows no tendency for the clay to localize in the larger crumbs, but the cultivated soil shows a distinct tendency for the clay to disperse and to reaggregate into granules of higher clay and organic content.

The Hagerstown series is old geologically and is derived residually from thick bedded rather pure limestones containing hydrated iron oxides. In the process of profile development the residual clay is rather completely aggregated into stable crumbs; hence these granules do not contain much more clay than

the whole soil in the forested area sample. The Hagerstown in bluegrass sod probably passed through a period of cultivation in its agricultural history during which it became dispersed and ultimately reaggregated into high clay containing granules. Hagerstown soil which has been devoted to profitable tobacco production continuously for 49 years shows the effect of this use in the much higher clay and organic matter content of the coarse aggregates than of the whole soil. Such use has not made for an increase in the number of stable aggregates, as reflected in the probable permeability index, which reveals that only 20.3 per cent of the soil is present either as primary particles or aggregates in the form of these two analysis fractions. Tillage has caused dispersion of the clay, which has reaggregated to form granules of this different constitution. Reaggregation of the clay soon after its dispersal has been aided by the very important biological effects of manure, which has been applied annually.

SUMMARY AND CONCLUSIONS

Water-stable granules were separated from the A_1 horizon of 11 Pennsylvania soil types represented by 15 forested and cultivated areas. A complete mechanical and organic matter analysis was made of the "hand-picked" granules and of the whole soil. The results permit the following conclusions:

In the majority of instances large stable granules contain a greater percentage of organic matter and clay than does the whole soil from which they were derived.

The increase in clay content of the granules is not offset by an equivalent decrease in any other single particle size fraction. The percentage of silt, sand, or gravel in the granules may be thus decreased.

The stability index, which is a measure of granule stability, is closely correlated with the organic content and the clay content of the soil.

The probable permeability is closely correlated with organic content but bears an insignificant relationship to the clay content.

Cultivation (broadly speaking) disperses existing granules, and the dispersed clay reaggregates to form granules higher in clay and organic content than the whole soil from which they were obtained.

The granules in young soil profiles seem to be formed and stabilized largely through the action of organic and biologic influences. Those in poorly drained profiles are formed chiefly by disintegration of more massive structural units and stabilized by the action of organic matter, whereas those in well-drained mature profiles, provided the latter have easily dispersible clay, possess granules which were formed by dispersion and reaggregation of the clay and the organic matter.

The granule genesis in the Hagerstown, Montalto, and Chester series may have been effected by the cementing action of hydrated iron oxides when the soil was developing. These granules are present in the forest soil but are gradually dispersed when the soils are brought under cultivation.

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ADSORPTION OF BARIUM AND HYDROXYL IONS BY SOILS AND MINERALS IN RELATION TO pH[1]

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In a previous paper (8) the writer proposed a method for the rapid estimation of base-exchange capacity and exchangeable hydrogen by means of barium chloride buffered at pH 8.2 with triethanolamine. Since it is of interest to know how far the base-exchange reactions have gone toward completion at pH 8.2, results are given in this paper dealing with the adsorption of barium by soils and minerals in which the cation concentration was held constant but the reaction was varied by the addition to triethanolamine and sodium hydroxide.

MATERIALS AND METHODS

Natural soil, silt and clay fractions of soil, and several minerals were studied. The soils used were from the following sources: the Portsmouth, Norfolk, and Wickham series and muck from the Coastal Plain of North Carolina; the Cecil series from the Piedmont Plateau; the Culvers, from Broome County, New York; the Lufkin and Eutaw, from Alabama; the Weld, from Colorado; the Yazoo, from East St. Louis, Illinois; the Perrine, from Homestead, Florida; and the Collington, from the Coastal Plain of New Jersey. The last was high in glauconitic sand which gave it a green color.

The silt and clay fractions were of particle size less than 0.02 mm., obtained by elutriation. After separation, the silt and clay were flocculated with hydrochloric acid and decanted; the residue was filtered and washed with 0.05 *N* HCl and finally washed with distilled water.

The peat was from the Florida Everglades Experiment Substation. It was leached with 0.05 *N* HCl and then washed with water. Humic acid was obtained from a sodium hydroxide extract of the peat, precipitated with HCl and washed with water.

The minerals were obtained from Ward's Natural Science Establishment, Rochester, New York. The lignite came from Sheridan County, Wyoming. After pulverization, the fraction smaller than 0.02 mm. was leached with 0.05 *N* HCl and finally washed with water. Halloysite var. indianaite was from Bedford, Indiana; pyrophyllite from Badin, North Carolina; fuller's earth

[1] Contribution from the department of agronomy, North Carolina Agricultural Experiment Station. Approved by the director as Paper No. 130 of the Journal Series.

from Attapulgus, Georgia; and chabazite from Kyogle, New South Wales. These materials were ground in a ball mill, and the fraction smaller than 0.02 mm. was leached with 0.05 N HCl and then washed with water. The bentonite came from Rock River, Wyoming. After grinding in a ball mill it was treated with HCl and allowed to diffuse through Alfrax extraction shells, additional amounts of acid being added until a hydrogen clay was prepared. The excess acid was then washed with distilled water in the same manner. Permutit (Folin) and kaolin are commercial products. Preliminary to the preparation of hydrogen clays in the usual manner (leaching with 0.05 N HCl) the kaolin, indianaite, pyrophyllite, montmorillonite, fuller's earth, and chabazite were digested twice in 5 per cent solutions of sodium carbonate in order to remove the free silica.

The soils and minerals were treated with increasing amounts of triethanolamine and sodium hydroxide in the presence of barium chloride, the concentration being held as constant as possible. A barium salt was selected because of the efficiency of the barium ion in replacing other cations. Triethanolamine was used because of its buffer properties between pH 7.2 and 8.6, which made it possible to obtain equilibrium within this range. It was assumed that because of its high molecular weight, 149.13, and its structure, $(HOCH_2CH_2)_3N + HOH = (HOCH_2CH_2)_3NH^+ \cdot OH^-$, the positive ions would not enter into an exchange reaction with the adsorptive complex in competition with barium, and that they would neutralize the hydrogen ions that are replaced by barium. These assumptions were proved to be correct by the preliminary results shown in table 1.

Fifty milliliters of 0.2 N $BaCl_2$ and 0.5 to 10 ml. of N triethanolamine or N NaOH were added to a weighed quantity of soil or other material. The amount of soil used depended upon the approximate clay content and varied from 5 to 25 gm. Of the clays and minerals, 2- to 5-gm. samples were used; and of the permutit, humic acid, and lignite, 1-gm. samples. Where less than 5 gm. was employed, a small amount of coarse acid-washed sand was added. This was necessary in order to cover the Berkefeld filter cylinder through which the suspensions were ultimately filtered. The suspensions were then shaken for 30 minutes in a mechanical shaker and filtered (7). The excess barium was leached with 40 to 50 ml. of distilled water and the combined extract and leachate made up to 100 ml. with distilled water. The original concentrations being known, the barium and the base adsorbed were determined in aliquots of the extract by difference. A detailed description of the volumetric determination of barium is given elsewhere (7, 8). The only modification in determining barium volumetrically has been the addition of a few milliliters of a buffered solution (pH 8.0) of triethanolamine acetate to the flask containing the standard sulfate solution. This made it possible to precipitate the barium always within the same narrow pH limits, irrespective of the large variations in pH of the extract.

The base adsorbed was determined on a 25- or 50-ml. aliquot by titrating

with 0.1 N HCl, using 1 drop of methyl red (0.04 per cent) and 2 drops of bromocresol green (0.04 per cent) as indicators.

The pH values were determined by means of a glass electrode. Measurements were made on the extracting solution and on the leached soil or materials. The soil and materials were taken up with 10 to 20 ml. of distilled water, stirred, and the pH was measured.

In the colorimetric determination of iron, aluminum, and silica, a uniform concentration of hydrogen ions is essential for best results. The aliquots containing various amounts of base were, therefore, first titrated with 0.5 N HCl, paranitrophenol being used as the indicator. Iron in solution was determined in a 10-ml. aliquot by acidifying with 0.5 N HCl and adding 1 ml. of a 2 per cent solution of potassium thiocyanate. The color thus developed in the presence of iron was measured in an electrophotometer.

TABLE 1

Influence of partly neutralized triethanolamine on the adsorption of barium

N TRIETHANOLAMINE ADDED (pH 8.2)	ADSORPTION OF BARIUM BY:			
	Perrine silt loam		Permutit	
	m.e./100 gm.	*pH*	*m.e./1 gm.*	*pH*
0	19.00	7.61	1.90	6.95
2	19.25	8.00	2.08	8.02
4	18.75	8.10	2.10	8.09
6	19.25	8.14	2.10	8.15
8	18.75	8.12	2.06	8.15
10	19.00	8.14	2.12	8.16

The soluble aluminum was determined in a 10-ml. aliquot in the presence of 2 ml. of 0.1 N acetic acid and 0.4 ml. of 0.05 per cent hematin (9). The color developed was measured in an electrophotometer.

Soluble silica was determined in a 20-ml. aliquot in the presence of 1 ml. of 0.1 N HNO_3 and 1 ml. of a 5 per cent solution of ammonium molybdate (11). Glass tubes were used for color comparisons against standard preparations.

RESULTS

In selecting triethanolamine as a base its influence on the adsorption of barium was first studied. By the procedure just described, 1 gm. of acid-washed silica powder was found to adsorb 0.108 m.e. of hydroxyl ions from a 0.04 N solution of triethanolamine and 0.168 m.e. in the presence of 0.2 N $BaCl_2$, an increase of about 55 per cent. The corresponding figures of H-permutit were 0.48 m.e. and 1.24 m.e., or an increase of about 158 per cent. Thus, any readily accessible hydrogen is neutralized by triethanolamine, but in order to neutralize exchangeable hydrogen a metal cation is essential for its replacement. The influence of increasing amounts of triethanolamine, partly neutralized with hydrochloric acid, on the adsorption of barium by calcareous

Perrine silt loam and permutit are given in table 1. The results clearly show no interference by the amine, provided the reaction is held constant. The amounts of triethanolamine which were added in the subsequent tests did not exceed 10 ml. of a normal solution. The reaction of the commercial triethanolamine is pH 10.6.

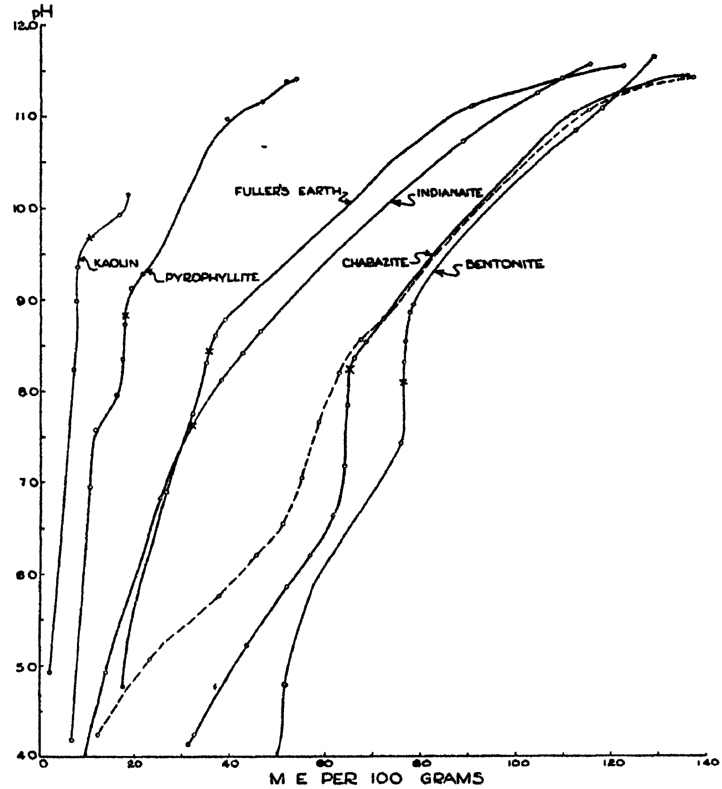

FIG. 1. ADSORPTION OF BARIUM BY MINERALS IN RELATION TO pH

The broken line represents the neutralization curve of hydrogen of chabazite. Each cross denotes the approximate pH at which the exchangeable hydrogen is neutralized.

Adsorption of barium by minerals

Adsorption of barium was measured for various minerals, some of which are considered in the literature as being present in the soil. These results are presented in figure 1.

Adsorption of barium by indianaite continually increases with increasing pH, but in the case of the other minerals it shows a pronounced maximum between pH 8.0 and 9.0. The pH values at which these breaks occur and their magnitude vary with the minerals. The neutralization curve of exchangeable hydrogen of chabazite, in figure 1, is representative of those obtained for the

other minerals. Neutralization of hydrogen for this mineral is virtually complete at pH 8.3. Above this pH value, adsorption of barium and hydroxyl ions takes place in about equivalent amounts. This applies to the other minerals, except that the pH value at which neutralization of hydrogen is accomplished varies with the different minerals, as indicated in figure 1.

Adsorption of barium by soils

Adsorption of barium by natural soils and by silt and clay fractions is shown in figure 2.

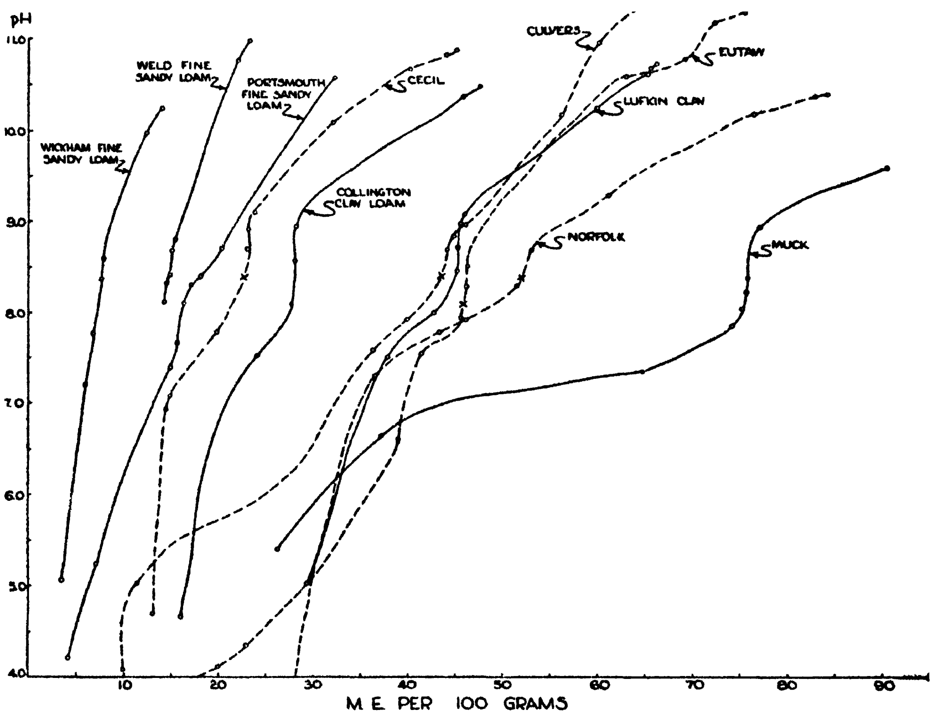

FIG. 2. ADSORPTION OF BARIUM BY SOILS IN RELATION TO pH

The solid lines represent the natural soils; the broken lines, the hydrogen-saturated fraction smaller than 0.02 mm. diameter particle size. Each cross denotes the approximate pH at which the exchangeable hydrogen is neutralized.

Adsorption of barium increases with increasing pH, with a break occurring between pH 7.8 and 9.0. The extent of this deviation and the pH limits at which this break occurs vary with the soil. It is very pronounced with Collington, Lufkin, Eutaw, and muck and is sufficiently distinct with the other soils. The neutralization of the exchangeable hydrogen by the hydrogen-saturated silt and clay fractions is accomplished between pH 8.0 and 8.8. Adsorption of barium and hydroxyl ions above this point continues to increase in essentially equivalent amounts.

In addition to the data presented in figure 2 adsorption measurements were made on Culvers gravelly silt loam, Norfolk fine sandy loam, Cecil clay loam, and Yazoo loam. Maximum adsorption of barium was obtained for the Culvers soil at pH 8.2, for the Norfolk at pH 8.2, for the Cecil at pH 8.6, and for the Yazoo at pH 8.4.

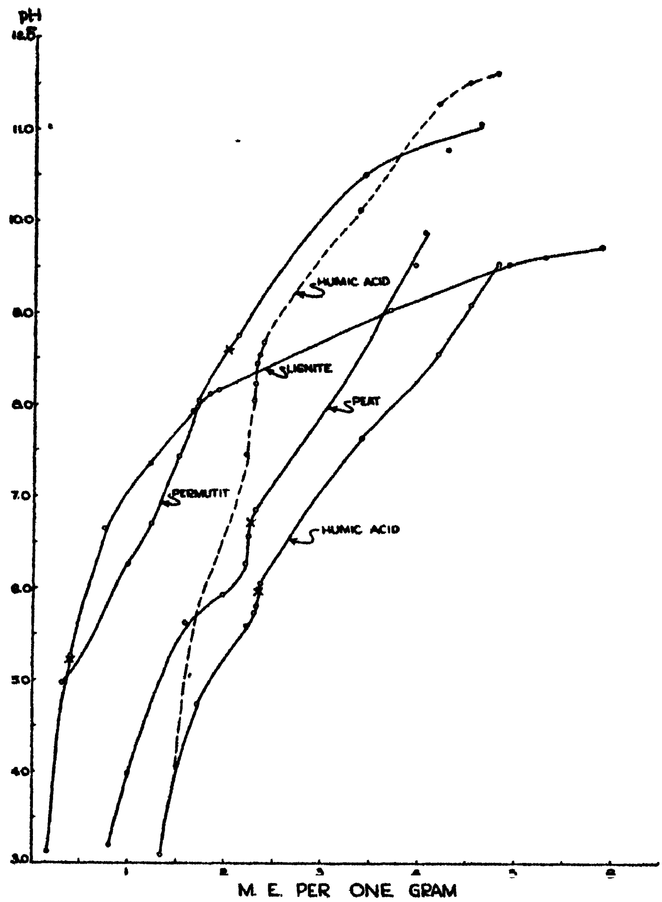

FIG. 3. ADSORPTION OF BARIUM BY LIGNITE, PEAT, HUMIC ACID, AND PERMUTIT

The dotted line represents the barium-adsorption curve of humic acid plotted against the pH of the extracting solution. Each cross denotes the approximate pH at which the exchangeable hydrogen is neutralized.

Adsorption of barium by lignite, peat, humic acid, and permutit

In figure 3 adsorption of barium by lignite, peat, humic acid, and permutit in relation to pH is shown. Adsorption increases with increasing pH in lignite and permutit, without showing a definite break in the curve. A definite maximum at pH 6.0 with humic acid and at about pH 6.8 with H-peat is, how-

ever, shown. Adsorption of barium by humic acid was also plotted against the pH of the extracting solution and is represented by the broken line in figure 3. Attention is directed to the large differences in pH of the leachate as compared to the leached humic acid. These differences were also appreciable for the H-peat, whereas they were small for the soils and minerals.

Neutralization of exchangeable hydrogen is accomplished at pH 6.0 for humic acid, at pH 6.8 for H-peat, and at pH 8.7 for permutit. Above these pH values adsorption of barium and hydroxyl ions continued to increase in approximately equivalent amounts. Equivalent adsorption of barium and hydroxyl ions by lignite was observed above pH 5.2.

Relation of pH to amounts of aluminum and silica in solution

Soluble aluminum was usually found in all minerals and soils in increasing amounts above pH 8.0. No aluminum was found between pH 4.5 and pH 8.0. Soluble silica was found in increasing amounts only above pH 10.0, with the exception of permutit, where it was found in appreciable amounts above pH 7.7, and fuller's earth, where it was found over the entire range of reaction. The fact that fuller's earth is a mixture of various minerals may account for the high amount of silica. It contains over 70 per cent silica and about 12 per cent aluminum oxide (6). Its mineral composition may include hydrated oxides of silicon and aluminum, and minerals such as smectite, malthacite, pyrophyllite, and montmorillonite. Traces of silica were measured over a wide range of reaction in pyrophyllite. The results with soil are substantially in agreement with those of Bradfield (2), who found aluminum in solution in increasing amounts only above pH 8.0 and below pH 4.5, whereas, in general, silica in solution was found only below pH 4.0 and above pH 10.0. (Data referred to in above paragraph are not included.)

DISCUSSION

From the results presented in this paper, it appears that adsorption of barium by most soils and minerals reaches a maximum coincident with the neutralization of the exchangeable hydrogen. The reaction at which this occurs varies with the soil or mineral.

Neutralization is accomplished at pH 6.0 for humic acid, at pH 6.8 for peat, at pH 7.9 for Eutaw, and at pH 8.2 for Norfolk. In the minerals, neutralization is virtually complete at pH 8.1 for bentonite, pH 8.3 for chabazite, at pH 8.7 for pyrophyllite, and at pH 9.6 for kaolin. Above these pH values, both barium and hydroxyl ions are adsorbed in increasing and in essentially equivalent amounts. They are adsorbed in approximately equivalent amounts by indianaite above pH 7.6, by silica powder above pH 7.9, and by lignite above pH 5.2. For these materials, a maximum adsorption of barium was not observed.

The adsorption behavior of barium and hydroxyl ions by silica may be explained, according to Jackson and Truog (5), on the premise that with in-

creasing hydroxyl ions, the silica probably splits the XSi-OSiX bonds into XSi-OH and XSi-Ba. The similar behavior of halloysite may be explained on the basis of its structure, which, according to Edelman, behaves like a real acid (4). He asserts that halloysite has three configurations: first, a sheet of O ions bound to Si; second, a sheet of OH ions bound to Al; and third, a sheet of OH ions bound to Si. The hydrogen of the OH group bound to Si, being more active, determines the extent of adsorption.

The data indicate that adsorption of barium by inorganic soils from 0.2 *N* solutions reaches a maximum or constant level between pH 8.0 and 9.0, and adsorption by organic soils reaches a maximum between pH 6.0 and 7.0. The base-exchange capacity and exchangeable hydrogen obtained with the proposed barium chloride–triethanolamine method buffered at pH 8.2 may be expected, therefore, to yield maximum values for most of our agricultural soils. These observations are also in agreement with the results obtained by Bradfield and Allison (3) in which a carbonation method was used. They obtained maximum values for base-exchange capacity for most soils between pH 8.1 and pH 8.4. For some soils, a system buffered at pH 8.4 or higher may give better results. A higher reaction, however, is not recommended where barium is used, since it involves secondary reactions such as the formation of barium carbonate. Also, an increase in reaction above pH 8.2 is accompanied by an increase in hydrolysis of some soils, as indicated by the increasing amounts of aluminum going into solution. Finally, it may be assumed that a maximum for base-exchange capacity is obtained at lower pH values, provided a great excess of hydrolizable salts, such as barium or ammonium acetates, is used. Such a procedure, although widely employed, does not lend itself to a rapid estimation of base-exchange capacity, since the adsorbed ions cannot be easily determined by difference, as in the proposed method.

The results, in general, indicate that measurements of cation adsorption in relation to pH serve more readily to characterize a soil than the use of titration methods, the results of which are usually represented by plotting the increments of base added against pH (1, 10). In the latter methods, the end-point for the complete neutralization of exchangeable hydrogen is difficult to observe, because of several factors, the most important of which are the admixture in the soil colloid of finely divided silica and the amphoteric character of aluminum. The nature of the adsorption reactivity of silica has been referred to. Because of the amphoteric character of the aluminum, the titration of its salts with a base shows increased buffer properties above pH 8.0 (12, p. 117), whereas the titration of sodium silicate with aluminum chloride shows virtually no buffer properties between pH 4.5 and 10.0. If only the activity of the hyxdroxyl ions is measured by the usual titration method, secondary reactions frequently mask the true end point for the neutralization of hydrogen.

The adsorption-capacity constant of the barium is probably influenced by mineralological structure, Si:Al ratio, and size of particles. These properties are interrelated in governing stability with reference to ease of hydrolysis (5).

In the artificially prepared permutit the stability is low, hence no significant adsorption constant may be expected. Kaolin, bentonite, and chabazite give a very pronounced adsorption constant and may be expected to be stable as verified by the small amounts of silica in solution. This stability may be decreased by grinding to near-molecular size, in which case the adsorption capacity constant may be expected to be less pronounced. Admixture of other minerals, particularly finely divided silica, influences this constant.

SUMMARY

Natural soils, hydrogen-saturated silt and clay fractions, peat, humic acid, and several minerals were treated with increasing amounts of triethanolamine and sodium hydroxide in the presence of a constant concentration of barium chloride. After shaking, leaching, and washing, the amounts of barium and hydroxyl ions adsorbed were measured volumetrically and the following results obtained:

Adsorption of barium by soils and several minerals reaches a maximum coincident with the neutralization of exchangeable hydrogen. The reaction at which this occurs varies with the soil or mineral, i.e., about pH 6.0 for humic acid, pH 6.8 for peat, pH 7.9 for Eutaw, pH 8.2 for Norfolk, pH 8.1 for bentonite, pH 8.3 for chabazite, pH 8.7 for pyrophyllite, and pH 9.6 for kaolin. Above these pH values both barium and hydroxyl ions are adsorbed in increasing and essentially equivalent amounts.

Maximum adsorption of barium by permutit, halloysite var. indianaite, silica, and lignite was not measurable. Equivalent adsorption of barium and hydroxyl ions by these materials occurred above pH 5.2 for lignite, pH 7.6 for indianaite, pH 7.9 for silica, and pH 8.7 for permutit.

From these results it is concluded that the barium chloride method buffered at pH 8.2 with triethanolamine should yield maximum values for base-exchange capacity and exchangeable hydrogen for most agricultural soils.

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CALCIUM- AND SULFATE-ION CONCENTRATIONS IN A SOIL RECEIVING EXCESS GYPSUM, AS INFLUENCED BY SEVERAL FACTORS[1]

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Solubility product effects are undoubtedly of great importance in determining the concentrations of various ions in the liquid phase of soils. Thus phosphate concentrations in soils have been shown (9) to be dependent, among other factors, upon both Ca- and H-ion concentrations. Almost any treatment of a soil with salts or acids designed to affect only one of these ions may, in addition, indirectly affect the other. To reduce the effects of pH changes to a minimum, the concentrations of Ca and SO_4 ions in the liquid phase of a soil to which an excess of gypsum had been added were chosen for study.

As a result of preliminary tests, it was found necessary to consider another factor in addition to the inverse relationships of Ca- and SO_4-ion concentrations; namely, the ionic strength of the solution, and the resultant effects on the activities of Ca and SO_4 ions in solution. Ordinarily, the ionic strength of the solutions in equilibrium with difficultly soluble salts may be low enough to be neglected. But the concentration of ions necessary to cause precipitation of $CaSO_4$ is so high that this factor is strongly brought into play.

MATERIALS AND METHODS

The soil used throughout these studies was a subsurface sample of Yolo fine sandy loam (7) from the agronomy plots at Davis. A 2-kgm. portion of this soil with an excess of gypsum added as C.P. $CaSO_4 \cdot 2H_2O$ was allowed to remain in contact with 1 liter of solution at 26°C. for 24 hours, during which stirring was frequent. Nine solutions were used with the following approximate concentrations: 0.49 *M* $CaCl_2$, 0.17 *M* $CaCl_2$, 0.07 *M* $CaCl_2$, distilled water, 0.08 *M* K_2SO_4, 0.16 *M* K_2SO_4, 0.18 *M* K_2SO_4, 0.25 *M* K_2SO_4, and 0.51 *M* K_2SO_4. The addition of the highest concentration of K_2SO_4 to the soil resulted in a much stiffer consistency of the mixture after standing an hour. The other

[1] Contribution from the Division of Agronomy, Davis, California. The writers gratefully acknowledge the help of R. M. Keefer, Division of Chemistry, Davis, in the preparation of the manuscript.

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eight apparently remained unchanged in this respect. By passing these suspensions through filter paper supported on glazed Büchner funnels, the respective 2:1 (soil: water) "equilibrium" extracts were obtained. Suitable aliquots of these were analyzed for Ca by the usual $KMnO_4$ titration of the precipitated oxalate (1), for Mg by the gravimetric determination as $Mg_2P_2O_7$ (1), and for SO_4 by the usual gravimetric method (1).

Similar studies were made using approximately the same solutions in contact with excess gypsum but without soil. After the excess gypsum was filtered off, Ca and SO_4 ions were determined.

To study the quantitative effect of increasing ionic strength on the solubility of gypsum, 2:1 "equilibrium" extracts were made from soils to which three different concentrations of KCl had been added. The Cl-ion concentration in these KCl solutions was the same as in the solutions of $CaCl_2$ used in the earlier part of this experiment.

Normally, soil systems in the field are subject to changes in acidity and in moisture content. To simulate the effect of biologically produced acids, such as HNO_3 and H_2SO_4, on the solubility of gypsum in soils, various concentrations of HCl were added to the soil containing an excess of gypsum. The resulting 2:1 extracts were then obtained as previously described. The effect of varying water contents on a soil system containing 0.17 moles of calcium chloride for each 2 kgm. of soil and an excess of gypsum was explored over a range of soil:water ratios varying from about 6:1 (approximately field capacity) to 1:5. The soil solution at the lowest moisture content was obtained by displacement in soil tubes (2); extracts for the others were obtained in the same way as previously for the 2:1 water extracts.

RESULTS AND DISCUSSION

The concentrations of Ca and SO_4 ions are plotted logarithmically in figure 1; those from the soil extracts, as curve B, and those from the pure solutions, as curve A. The agreement[4] between our experimental results and those in the literature was good in curve A, except for one point (8), namely, with the 0.25 *M* K_2SO_4. The clear filtrate from this mixture slowly developed a precipitate on standing, indicating thereby an initial supersaturated solution (4). Conditions present in this system also undoubtedly favored the formation of complex ions involving K_2SO_4 and $CaSO_4$ (4).

In comparing the tabular material from which the curves A and B in figure 1 were plotted, several points of interest were apparent, though noticeable on the graph only by detailed consideration of the points. The Ca-ion concentrations found in the soil "equilibrium" extracts where $CaCl_2$ and distilled water were used, were lower than in the corresponding extracts without soil, whereas the

[4] This agreement is the basis for assuming that equilibrium, except as noted in the text, was obtained in the "equilibrium" extracts between the ions in solution and solid-phase gypsum. Undoubtedly equilibrium between the solution and the soil was approached but not completely attained in the 24-hour period of contact.

SO_4-ion concentrations were higher. These results indicate that some Ca ions were removed from solution by cation exchange reactions. This removal allowed a new equilibrium to be approached or established, which according to the solubility product law allowed more gypsum to enter solution, thus giving a higher value for SO_4 ions. In the solutions to which K_2SO_4 was added, the Ca-ion concentration was higher in those solutions which had been in contact with the soil, because the added K ions replaced Ca ions present in the cation

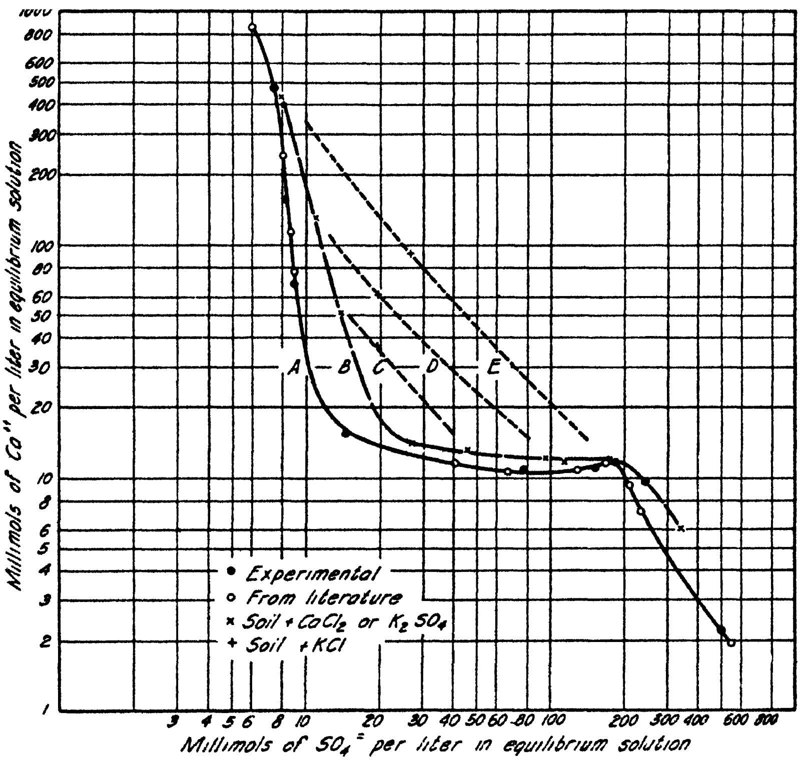

FIG. 1. CONCENTRATIONS OF Ca AND SO_4 IONS IN SYSTEMS CONTAINING EXCESS GYPSUM

Curve A, in solutions with $CaCl_2$ or K_2SO_4; curve B, in "equilibrium" soil extracts with $CaCl_2$ or K_2SO_4; curves C, D, and E, in "equilibrium" soil extracts with equivalent total anionic concentrations: C, with 143; D, with 356; and E, with 1080 m.e. per liter.

exchange complex. This increased Ca concentration undoubtedly caused a decrease in the concentration of SO_4 ions found in the "equilibrium" solution, thereby in part accounting for the higher SO_4 concentration found in the pure solutions than in the corresponding soil extracts. The data for experimental points (+) in figure 1 were obtained by adding to 2-kgm. portions of the soil containing excess gypsum, respectively, 1 liter of the following concentrations of KCl: for curve C, 0.143 *M* KCl; for curve D, 0.356 *M* KCl; and for curve E, 1.08 *M* KCl. Each of these curves represents Ca and SO_4 concentrations in

solutions with the same equivalent total (i.e., Cl plus SO_4) anionic concentrations computed, for the most part, from data used to plot curve B.

The Ca and Mg concentrations in the "equilibrium" extracts from the KCl-treated soil increased with the amount of KCl added, in accordance with normal cationic exchange phenomena. In the treatment with the largest amount of KCl, the highest concentrations of both Ca and SO_4 occurred. The K and Cl ions remaining in solution and the Mg ions entering solution because of cationic exchange have here increased the solubility of the gypsum.

The slight change in SO_4 concentration in the extract of the two lower KCl concentrations (cf. fig. 1 "+" points on curves C and D) indicated a balance between the increase in solubility brought about by salts with no ions common with gypsum and the decrease in solubility in the presence of an increasing amount of a common ion (Ca^{++}) which originated from the soil colloids by cationic exchange with the K ions added.

TABLE 1

Mg- and Cl-ion concentrations in 2:1 "equilibrium" soil extracts

Values in milliequivalents per liter

SALT ADDED	APPROXIMATE AMOUNT	CONCENTRATION OF IONS		SALT ADDED	APPROXIMATE AMOUNT	CONCENTRATION OF IONS	
		Mg	Cl			Mg	Cl
None	. . .	30	trace		140	70	142
				$CaCl_2$	340	106	348
	160	50	trace		980	146	980
	320	86	trace				
K_2SO_4	360	94	trace		143	82	143
	500	122	trace	KCl	356	100	356
	1020	146	trace		1080	108	1080

The series of approximately straight parallel lines, C, D, and E, of figure 1 drawn through points of equivalent total anionic concentrations indicate an approximately constant ion concentration product for Ca and SO_4 ions in a series of solutions of approximately constant ionic strength. One factor preventing the lines C, D, and E from being straight is the inability to represent in this figure the effect of the concentrations and resultant ionic strength of all cations present on the activity coefficients of Ca and SO_4 ions.

The Mg- and Cl-ion concentrations determined in the various "equilibrium" extracts are reported in table 1. The Mg^{++} found in the "equilibrium" extracts, increasing with increasing salt concentrations added, undoubtedly originated by exchange from the replaceable Mg of the soil. The data in table 1, together with the data plotted in figure 1, made it possible to compute later the total ionic strength of each of the "equilibrium" extracts.

The equilibrium for gypsum in a saturated solution can be expressed by the following equation:

$$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{++} + SO_4^{--} + 2H_2O$$

Let:

$S.P.\ \infty$ = the solubility product of gypsum at infinite dilution.
A = activity of the ion
γ = activity coefficient of the ion
$\gamma \pm$ = mean activity coefficient of the ions
$I.C.P.$ = ion concentration product
= $(Ca^{++})\ (SO_4^{--})$ for gypsum
μ = ionic strength of the solution

Then:

$$S.P.\ \infty = A_{Ca^{++}} \cdot A_{SO_4^{--}} = \gamma_{Ca^{++}}(Ca^{++}) \cdot \gamma_{SO_4^{--}}(SO_4^{--}) \quad \ldots\ldots 1$$

$$\log S.P. = \log (Ca^{++})(SO_4^{--}) + \log \gamma_{Ca^{++}} \cdot \gamma_{SO_4^{--}}$$
$$= \log (Ca^{++})(SO_4^{--}) + \log \gamma_{\pm}^2 \quad \ldots\ldots\ldots\ldots 2$$

The simplified expression for solubility product written without the activity coefficients for the ions can be used only at infinite dilution, in which case the activity coefficients are equal to unity.

Previous workers (6, p. 201) have shown that

$$\log \gamma_{\pm} = f\sqrt{\mu} \quad \ldots\ldots\ldots\ldots 3$$

The ionic strength, μ, of each equilibrium solution was calculated from the general formula as given by Lewis and Randall (5, pp. 373–374) for dilute solutions. Though it is a common practice among chemists (3) to plot, by adapting equation 3, the negative logarithm of the activity coefficient against $\sqrt{\mu}$ as a means of comparing the solubility of a salt in solutions of different ionic strengths, adequate comparisons of the solubilities can be made by plotting the log $I.C.P.$ against $\sqrt{\mu}$. These two types of comparisons are related by transposing and generalizing in equation 2 thus:

$$\log I.\ C.\ P. = \log S.\ P.\ \infty - 2 \log \gamma_{\pm} \ldots\ldots\ldots\ldots 4$$

In figure 2 the log $(Ca^{++})\ (SO_4^{--})$ is plotted against $\sqrt{\mu}$. From equation 4

$$\gamma_{\pm}^2 = \frac{S.\ P.\ \infty}{I.\ C.\ P.} \quad \ldots\ldots\ldots\ldots 5$$

Lewis and Randall (5, p. 376) gave 0.358 for the mean activity coefficient of Ca and SO_4 ions in a saturated solution in pure water. The corresponding value of $\sqrt{\mu}$ for gypsum under these conditions is given as 0.25 in figure 2. Siedell (8) gave 15.295 millimols per liter as the solubility of gypsum. Using .0153 as the concentration of Ca and SO_4 ions and substituting in formula 5:

$$(.358)^2 = \frac{S.\ P.\ \infty}{(.0153)^2}$$

$$S.\ P.\ \infty = 3.00 \times 10^{-5}$$

From this formula and the data plotted in figure 2, it is possible to calculate the approximate activity coefficient for $CaSO_4$ at any point on curves A and C. For example in the presence of the highest concentration of $CaCl_2$ ($\sqrt{\mu} \cong 1.2$),

$$\gamma_\pm^2 = \frac{3.00 \times 10^{-5}}{(.465)(.0074)}$$

$$\gamma_\pm^2 = 0.00872$$

$$\gamma_\pm = 0.093$$

Curve A (cf. fig. 2) represents the results calculated from solutions resulting after the addition of K_2SO_4 to $CaSO_4$ both in pure solutions and in the presence

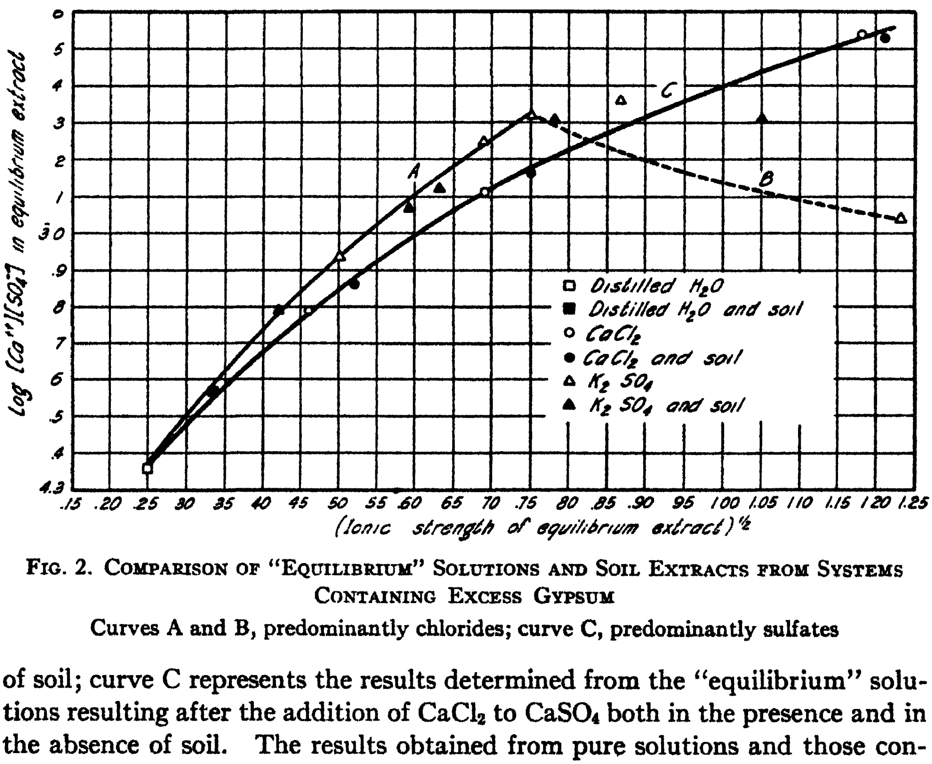

FIG. 2. COMPARISON OF "EQUILIBRIUM" SOLUTIONS AND SOIL EXTRACTS FROM SYSTEMS CONTAINING EXCESS GYPSUM

Curves A and B, predominantly chlorides; curve C, predominantly sulfates

of soil; curve C represents the results determined from the "equilibrium" solutions resulting after the addition of $CaCl_2$ to $CaSO_4$ both in the presence and in the absence of soil. The results obtained from pure solutions and those containing soil with an addition of the same salt can be compared with a reasonable degree of accuracy because the difference in ionic strength between any two solutions compared is small and the salts present in each are not materially different.

The fact that the values obtained from both the pure solutions and from the solutions containing soil fall on the same smooth curves when log (Ca^{++}) (SO_4^{--}) is plotted against $\sqrt{\mu}$ should be conclusive evidence that differences in solubility of gypsum in pure salt solutions and in solutions containing soil are due mainly to differences in the ionic strengths of the solutions.

The deviation of the two points (cf. curve B, fig. 2) from the plotted curve is, undoubtedly, due to supersaturation and the formation of complex compounds, as previously mentioned (4).

The Ca, SO_4, and Mg concentrations found in the 2:1 "equilibrium" extracts after the addition of increasing amounts of acid are given in table 2. The pH values for the extracts given in the table were determined by means of the quinhydrone electrode. The Ca and Mg concentrations increased in the extracts directly with increasing amounts of added acid as a result of the exchange of Ca and Mg ions for H ions. The slight change in SO_4 concentration accompanying a large change in Ca concentration can be attributed to an approximate balance between the increasing solubility of gypsum in the presence of increasing amounts of acid and of $MgCl_2$ (i.e., increasing ionic strength) and a decreasing solubility of gypsum in the presence of increasing concentrations of Ca ion. Appreciable quantities of the SO_4 determined at the higher concentrations of HCl were probably present in the extract as HSO_4 ions.

TABLE 2

Extracts from a saturated soil-water-gypsum system after addition of different amounts of hydrochloric acid

Concentrations in millimoles per liter

EQUIVALENTS OF ACID ADDED TO SYSTEMS	pH OF EXTRACT	ANALYSIS OF "EQUILIBRIUM" SOLUTIONS FROM 2:1 EXTRACT		
		Ca	SO_4	Mg
None	6.7	14.0	27.0	15.0
.05	6.4	21.6	21.3	25.4
.15	3.9	43.7	17.8	46.6
.40	2.6	95.5	23.4	93.3
1.00	.93	133.0	23.5	106.0

The effects of varying soil-water ratios on the Ca-, Mg-, and SO_4-ion concentrations in a soil containing 0.17 mole of $CaCl_2$ for each 2 kgm. of soil are reported in table 3. The small change in concentration of SO_4 ion in the presence of increasing concentrations of Ca ion can be explained by the increasing solubility of gypsum in the presence of increasing concentrations of Mg ion, which varied almost directly with the Ca-ion concentration. As the soil-water ratio decreased, the concentration of readily soluble salts also decreased, resulting in a progressively smaller effect on the solubility of gypsum.

The approximately direct proportion existing between the SO_4 ion remaining in solution and the amount of water present becomes evident when the millimoles per kilogram of soil are compared (cf. table 3). The deviations from a true direct proportion, as would be expected from a very slightly soluble salt in water, are accounted for by the ionic strengths resulting from the other electrolytes in the soil, concentrations of which change with the soil-water ratio.

The differences in the total amounts of SO_4 in the 1:1 and 1:2 extracts, and

between the 1:2 and 1:5 extracts can very nearly be accounted for by the solubility of gypsum in the added amount of water. Also, the difference in equivalents of SO_4 per kilogram of soil in any two successive extracts was approximately equal to the difference in equivalents of Ca present (cf. table 3, columns on the right), whereas the Mg present remained nearly constant. The principal changes, then, were caused by the dissolving of more gypsum and by the occurrence of a small amount of cationic exchange as the soil:water ratio was decreased. Since the amount of soluble Ca which had originated from gypsum was small when compared with that added in a readily soluble form

TABLE 3

Effect of variations in the soil-water ratios on the concentrations in "equilibrium" solutions and amounts of dissolved ions per kilogram of soil containing excess $CaSO_4 \cdot 2H_2O$ and 0.085M $CaCl_2$

MOISTURE ON AIR-DRY BASIS	ANALYSIS OF DISPLACED SOIL SOLUTION OR WATER EXTRACT					
	Millimoles per liter of solution			Millimoles per kgm. air-dry soil		
	Ca	SO_4	Mg	Ca	SO_4	Mg
per cent						
15.5	370	9.12	145.5	67.7	1.7	26.6
50	131	11.1	53.0	65.5	5.6	26.5
100	68.0	12.0	26.3	68.0	12.0	26.3
200	40.5	13.0	14.0	81.0	26.0	28.0
500	24.1	14.2	6.33	120.5	71.0	31.6

such as $CaCl_2$, little variation was expected in the amount of soluble Ca from a given quantity of soil even with rather large variations in the soil-water ratios.

SUMMARY

Solubility studies were made by allowing 2 kgm. of soil, containing an excess of gypsum, to remain in contact with 1 liter of solution which was frequently stirred. Nine solutions were used in the preliminary experiments—distilled water alone, three with varying concentrations of $CaCl_2$, and five with varying concentrations of K_2SO_4. Parallel studies, in the absence of soil, were made by allowing each of the nine solutions to remain in contact with an excess of gypsum.

The effect of changing ionic strength on the solubility of gypsum was approached by making 2:1 extracts from soils to which KCl solutions had been added. A comparison of the extracts of equivalent total anionic concentrations contained when calcium chloride, potassium sulfate, or potassium chloride was added, indicated an approximately constant ion concentration product for gypsum in solutions of equal ionic strength, and showed the effect of increasing ionic strength on the solubility of gypsum.

To simulate the effect of biologically produced acids on the solubility of gypsum in soils, because of the calcium and other ions brought into solution,

various concentrations of HCl were added to lots of soil containing an excess of gypsum.

The effect of varying water content on a soil system containing a given amount of calcium chloride and an excess of gypsum was explored over a wide range of soil-water ratios. The concentrations of Ca and SO_4 ions found are, within reasonable limits, explicable in terms of solubility-product and ionic-strength phenomena.

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STUDIES ON THE CERULEOMOLYBDATE DETERMINATION OF PHOSPHORUS[1]

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Since Truog and Meyer (8) presented their modification of the Denigès (ceruleomolybdate) method for the colorimetric determination of phosphorus, it has been used with various modifications for many kinds of phosphorus studies. Several important investigations have been reported concerning the effect of various factors on the results obtained with the method (1, 2, 4, 6). The suggested changes in procedure, though applicable to all situations, have not been incorporated into one single method. Furthermore, with the introduction of the photoelectric colorimeter, greater accuracy has been made possible, requiring a more rigid investigation of factors that previously could not be studied or their effect measured so carefully as with this new facility. It is the purpose of this paper to present briefly the results of such studies, to compile briefly contributions made regarding the preparation and storage of the reagents, and to develop a satisfactory method capable of speed and accuracy with great flexibility in meeting the requirements for various phosphorus analyses of soils and plant material.

The method investigated is that outlined by Truog and Meyer, with slight modifications. The modifications discussed in this paper were made either by other workers or by the writer as the result of necessary adjustments in order to adapt the method to analysis of soils and plant material. A Klett-Summerson (7) photoelectric colorimeter was used in conducting the investigations.

EXPERIMENTAL

A colorimetric method should be adaptable to a wide range of conditions, particularly to the determination of phosphorus in acid and alkaline extractions and solutions and in solutions containing excesses of magnesium oxide from the magnesium nitrate often used in ashing organic substances. The reaction under all these conditions could be corrected with NH_4OH or H_2SO_4. The

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effect of concentrations of approximately 1,600, 3,200, and 6,400 p.p.m. $(NH_4)_2SO_4$ upon the intensity of color, rate of development, and duration of maximum color was investigated under concentrations of phosphorus ranging from 0.05 to 2.00 p.p.m. The results are recorded in table 1. The average deviation for the mean of 15- and 20-minute readings with the three different concentrations of $(NH_4)_2SO_4$ showed that no appreciable differences existed. The mean of the average deviations for phosphorus concentrations of 0.05 to 0.25 p.p.m. was 1.34 per cent. The mean of the average deviations for all concentrations above 0.25 p.p.m. was 0.73 per cent. Similar mathematical treatment of all readings from 15 to 45 minutes gave the mean of average deviation of the 0.05 to 0.25 p.p.m. of phosphorus as 2.9 per cent. The mean of average deviations in the range of 0.5 to 2.00 p.p.m. of phosphorus was 1.0 per cent. In view of the fact that agreement of duplicates within 5 per cent is considered satisfactory, these deviations are not in any case serious. The greater deviations at the lower concentrations may be attributed in large part to slight variations in the tubes, to errors in reading, and to lack of sensitivity of the instrument to these values.

TABLE 1

Effect of concentration of $(NH_4)_2SO_4$ and of time after addition of $SnCl_2$ upon the photoelectric values of the ceruleomolybdate

P CONCENTRATION	AVERAGED READINGS* (DIAL VALUES) AFTER 15 AND 20 MINUTES FOR DIFFERENT CONCENTRATIONS† OF $(NH_4)_2SO_4$					READINGS‡ IN 5-MINUTE INTERVALS 15 TO 45 MINUTES	
	1,600 p.p.m.	3,200 p.p.m.	6,400 p.p.m.	Average	Average deviation	Average dial value	Average deviation
p.p.m.					*per cent*		*per cent*
0.05	26.6	27.0	27.1	26.9	0.75	25.9	3.7
0.10	45.5	44.3	46.6	45.5	1.68	45.7	2.4
0.25	103.8	107.4	107.8	106.3	1.60	103.4	2.5
0.50	200.8	199.8	201.3	200.6	0.28	197.0	1.3
0.70	272.	274.	267.	271.	0.99	268.	1.4
1.00	384.	391.	385.	387.	0.78	386.	0.9
1.25	484.	493.	485.	487.	0.75	486.	0.8
1.50	595.	583.	588.	589.	0.74	588.	0.6
1.75	680.	690.	680.	683.	0.63	683.	1.0
2.00	800.	819.	815.	811.	0.95	811.	0.9

* Readings here represent the average of duplicate readings obtained after 15 and 20 minutes for each concentration of $(NH_4)_2SO_4$ following the addition of $SnCl_2$.

† The concentrations of $(NH_4)_2SO_4$ represent neutralization of 4, 8, and 16 drops from the burette of 1:1 NH_4OH per 100 ml. of test solution.

‡ Readings represent the average of duplicate readings of all concentrations and of all 5-minute periods from 15 to 45 minutes, after the addition of $SnCl_2$.

The data indicate that no effect upon the rate of development of the color, its ultimate intensity, or its stability could be attributed to the variations in concentration of ammonium salt. The early fading noted by Truog and

Meyer (8) under visual observation was not evidenced by these data. In fact, the full intensity of color as measured by photoelectric means was not reached in concentrations of 0.25 p.p.m. or less until approximately 20 minutes after the stannous chloride was added. At concentrations of 0.50 to 1.00 p.p.m. of phosphorus, the maximum color was reached in about 10 minutes, and fading took place rather slowly for the next 50 minutes. The color intensity for concentrations greater than 1.00 p.p.m. reached its maximum in 5 to 10 minutes and remained almost constant for an hour. On the basis of these data, readings after the 15- to 20-minute interval seemed to give the most consistent results over the whole range of concentrations and was most adaptable to routine analysis.

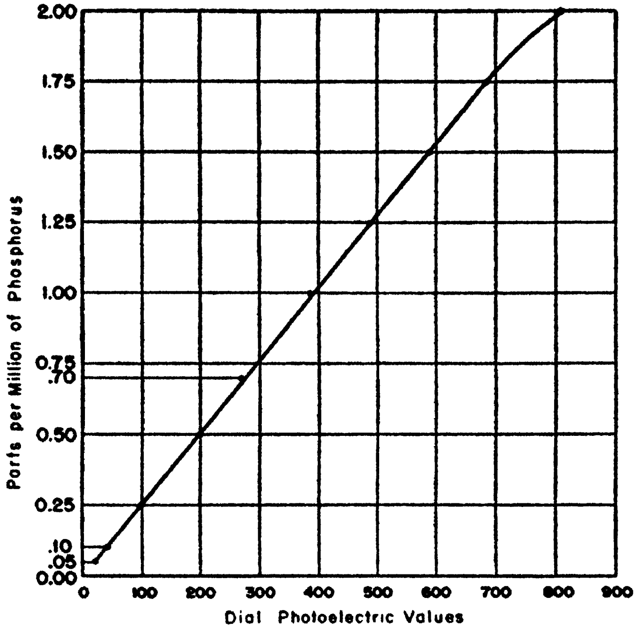

FIG. 1. PHOTOELECTRIC VALUES FOR VARIOUS CONCENTRATIONS OF PHOSPHORUS

Figure 1 is a graphic summary of the 15- and 20-minute readings given in table 1 for the mean values of the three concentrations of ammonium salt. The straight line which holds for concentrations of 0.05 to 1.75 p.p.m. on this particular instrument proved the conformity of the results within this range to Beer's law. (Subsequent tests on a similar instrument showed conformity only to 1.25 p.p.m., which indicated that it may be in part dependent upon the instrument.)

As suggested by Dickman and De Turk (3), the pH of the test solution was adjusted in these tests with para-nitrophenol as indicator. The pH of 30 test solutions which had been prepared without anticipation of checking their reaction was determined with a glass electrode subsequent to reading their

color values. The mean value for the pH of the test solution was 0.85 and the average deviation was only 0.95 per cent. This small deviation was obviously negligible in its effect on results.

Studies were conducted to ascertain the maximum concentrations of $(NH_4)_2SO_4$ and $MgSO_4$ which had no appreciable effect upon the color test. These are summarized in table 2 and expressed as parts per million of the sulfate ion in each case for comparison. Likewise, the milliequivalents of sulfate salt per 50 ml. of test solution are stated. With both sulfate salts, the maximum concentration of sulfate ion permissible was 4,360 p.p.m. or 4.52 m.e. per 50 ml. of test solution. This was approximately twice as great as the concentrations studied and reported in table 1. At this concentration the error due to the salt was 2 to 2.5 per cent whereas the error at half the above concentration was about 1 per cent. These errors are involved only if the constant, or curve, for deriving the phosphorus content is taken from values established by the use of standards containing inappreciable amounts of the

TABLE 2

Effect of sulfate salts upon colorimeter reading in phosphorus determination

(Mean of readings taken 15 and 20 minutes after addition of $SnCl_2$)

CONCENTRATION OF ADDED SO_4^{--} IN FINAL SOLUTION.	PHOTOELECTRIC COLORIMETER DIAL VALUES IN SOLUTIONS CONTAINING 1 P.P.M. OF PHOSPHORUS AS ORTHOPHOSPHATE					
	None	1,090 p.p.m. / 1.1 m.e.*	2,180 p.p.m. / 2.3 m.e.	4,360 p.p.m. / 4.5 m.e.	34,880 p.p.m. / 36.2 m.e.	69,760† p.p.m. / 72.3 m.e.
$(NH_4)_2SO_4$	400	400	405	410	460	475
$MgSO_4$..........	400	402	405	408	500	600

* Per 50 ml. of test solution.

† Blank reading (reagents minus P) gave 21 and 122 for $(NH_4)_2SO_4$ and $MgSO_4$, respectively, at this concentration.

sulfate salt. *Where the aforementioned concentrations are likewise used in standards for the establishment of the constant or factor, no error is involved.* Indeed, if the standards contained the same concentrations as those used in the tests, even the higher concentrations would not likely be objectionable. Studies on the color development in the presence of these salts indicated similar behavior with time to that given in table 1.

These studies demonstrated the great flexibility of the method. In consideration of the dilutions of 10 to 1,000 times made from the original extracting solutions or from the magnesium nitrate used in ignition, it is evident that high original concentrations are permissible within the limitations of this test.

METHOD

Pipette an aliquot of the phosphorus solution into a 50-ml. volumetric flask. Adjust the aliquot by dilution to contain 0.002 to 0.07 mgm. of phosphorus as orthophosphate. Add 1 or 2 drops of the para-nitrophenol indicator solu-

tion to the aliquot. Fill the flask at least half full with distilled water. Add a solution of 1:1 NH_4OH dropwise from a burette until the aliquot turns yellow. Then back-titrate the solution dropwise with 2 *N* H_2SO_4 until the yellow color just disappears. Add 2 ml. of the ammonium molybdate-sulfuric acid solution and make up to volume with distilled water. Thoroughly mix and transfer to a 125-ml. Erlenmeyer flask. Measure $SnCl_2$ solution in drops, add an amount equivalent to 0.23 ml., and mix thoroughly when the test is to be made. Make the photoelectric colorimeter readings 15 to 20 minutes after the addition of the $SnCl_2$. For routine analysis a range in temperature of the test solutions from 20° to 25°C. is permissible, provided the standards for establishing the curve, or factor, were run at 22° to 23°C.

Ammonium molybdate-sulfuric acid solution. Dissolve 25 gm. of C. P. $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$, in 200 ml. of water heated to 60°C. Dilute 275 cm. of concentrated, arsenic-free H_2SO_4 to 800 ml. Cool both solutions, then pour the molybdate solution slowly with stirring into the H_2SO_4. After cooling, dilute to exactly 1,000 ml. (8). If stored in a resistant glass bottle and protected from the light, it will remain unchanged indefinitely (5). For convenience in use and for protection of this reagent, the 1:1 NH_4OH, and the 2 *N* H_2SO_4, these solutions should be delivered from some kind of automatic burette.

Para-nitrophenol indicator solution. Dissolve 0.5 gm. of solid para-nitrophenol in 100 ml. of distilled water. Store in an indicator bottle with a dropper (3).

Standard phosphate solution. Dissolve 2.1965 gm. of dry, C. P. KH_2PO_4 in distilled water. Add 5 ml. of 50 per cent by volume H_2SO_4 and dilute to 1 liter. This solution contains 500 p.p.m. of phosphorus as orthophosphate. A solution of this concentration when placed in a tightly stoppered reagent bottle will keep indefinitely. Standards of 5 p.p.m. of phosphorus prepared by dilution of the stock solution 100 times should be made up daily as needed, for the diluted solution does not keep, and neither is it effectively preserved by toluene (5).

Stannous chloride solution. Dissolve 10 gm. of C. P. $SnCl_2 \cdot 2\ H_2O$, in 100 ml. of redistilled 6 *N* HCl, and dilute to 500 ml. with recently boiled distilled water. Titrate aliquots by the iodimetric method to determine the percentage of stannous chloride in the solution. (If the purity is less than 90 per cent, a fresh stock should be obtained.) Dilute the solution with 1.2 *N* HCl to contain 1 per cent $SnCl_2$ and store under hydrogen.

Smith et al. (6) demonstrated the importance of using a stannous chloride solution of high purity and of using a very definite amount of the reagent. In accordance with their plan of storing the stannous chloride under hydrogen as a preservative, a simple apparatus was devised and is shown in figure 2. It consists of a hydrogen generator connected directly to a reservoir of stannous chloride. As designed, it functioned perfectly. The glass beads retarded rapid changes in solution level of the HCl in the generator, yet at all times an adequate flow of hydrogen was assured by action of the HCl on the zinc bar

to permit withdrawal of the stannous chloride, either dropwise or in large aliquots for analysis. The apparatus, equipped with heavy rubber connections (Garlock No. 1 with $\frac{1}{16}$-inch walls) treated with a heavy coat of quick-drying varnish, had effectively preserved the stannous chloride against oxidation for more than 5 months at this writing. The stannous chloride reservoir was a brown bottle. Every precaution was taken to remove all air before the system was closed, and the stannous chloride solution was prepared just prior to its

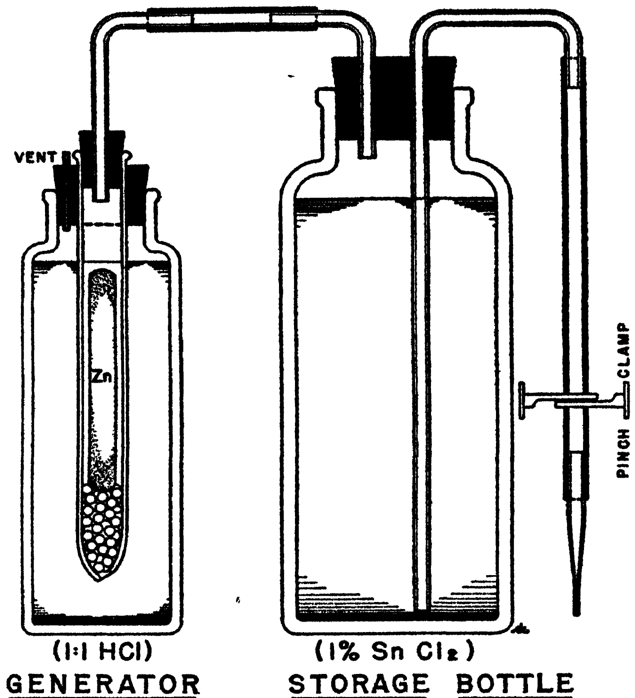

FIG. 2. APPARATUS FOR STORAGE OF STANNOUS CHLORIDE UNDER HYDROGEN

storage under hydrogen. It was found that when the solution was exposed to the air for 16 hours the stannous tin decreased by 20 per cent.

SUMMARY

Several modifications of the Truog and Meyer method for the colorimetric determination of phosphorus were investigated.

By the use of a Klett-Summerson photoelectric colorimeter an agreement of the test to Beer's law was demonstrated for 0.05 to 1.75 p.p.m. of phosphorus as orthophosphate.

It was demonstrated that as much as 4.5 m.e. of ammonium or magnesium sulfate may be present in 50 ml. of the final test solution without seriously affecting the results. At higher concentrations, the magnesium ion apparently exerted a greater effect upon color development than the ammonium ion.

An apparatus was illustrated for the effective preservation of the stannous chloride solution under hydrogen for an unlimited period of time.

Consideration was also given to the preparation and storage of the other reagents, thus ensuring consistent results over a long period and providing for speed and accuracy in routine analysis.

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THE SIGNIFICANCE OF OXYGEN IN NUTRIENT SUBSTRATES FOR PLANTS: I. THE OXYGEN REQUIREMENT[1]

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Although the necessity of oxygen for the growth of plants has been known since 1668 (2), comparatively little study has been made of the quantitative aspects of the growth of plants in relation to the supply of oxygen. Recent work has focused attention upon the oxygen supply to the roots as an important factor in the nutrition of the plant.

A series of papers will present the results of investigations of the metabolism of plants under conditions of constant oxygen tensions in the substrate. This paper, the first of the series, discusses the effects of such a maintained oxygen supply to the roots upon the growth of different species of plants. Descriptions of the methods employed are given in this paper.

All the experiments described herein were conducted by a modification of the standard continuous flow method (6) which permitted the isolation of the root system and of the gas space above the nutrient solution from contact with the outside air. Thus, a definite oxygen tension could be maintained around the roots by aeration of the nutrient solution with a gas mixture which contained the proper proportion of oxygen to nitrogen to give the desired oxygen tension in equilibrium with the dissolved gases at the prevailing temperature.

The gases were obtained either from cylinders of oxygen and of nitrogen or from a commercial mixture of these gases, or by dilution of the pure gas with the proper proportion of air. The dilution was made quantitatively by controlling the ratio of the volumes of the component gases. A direct-reading flowmeter (4) was placed in the gas train of each gas to measure the velocity of flow just before the gases joined in the mixing reservoir. As the gases were maintained under the same pressure by equal heads of water in escape valves, the proportionate mass of each component gas was determined by the ratio of the velocities of flow of the gases.

Temperature changes will not affect the ratio of the volumes of the component gases but will influence the solubility of oxygen under any one oxygen tension. Thus the actual concentration of dissolved oxygen was subject to fluctuations of about 25 per cent maximum deviation from the calculated values for 25°C. and 760 mm. pressure. Since the differences between the

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of plant physiology.

oxygen tensions used in the different treatments were very large and extreme fluctuations in temperature were not encountered in this work, the temperature factor should not seriously affect the general conclusions regarding the influence of oxygen tension on plant metabolism.

Figure 1 shows the details of the apparatus used for growing the plants with continuous nutrient solution flow and with roots in contact with a definite oxygen tension. A 2.6-liter bottle (*A*) was used as the culture vessel, being fitted with a large flat rubber stopper (*B*) to make a gas-tight closure of the neck of the bottle. Holes were drilled in the stopper for gas and solution inlet and outlet tubes, and for the supports for the plants (three or six per jar).

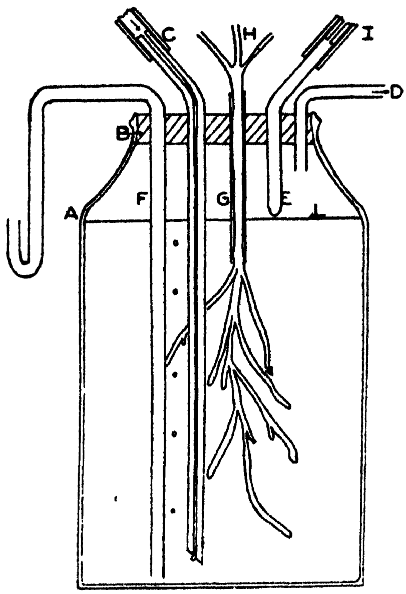

FIG. 1. DIAGRAM OF CULTURE VESSEL AND APPARATUS, SHOWING ONE PLANT WITH THE ROOT SYSTEM ISOLATED FROM THE ATMOSPHERE

The supports for the plants were the narrow glass tubes (*G*) (7 cm. long and 0.5 cm. bore) which enclosed the hypocotylar region of the seedling (*H*). The tubes extended from the upper surface of the rubber stopper to about 2 cm. below the level (*L*) of the solution in the jar, thus forming a water seal around the hypocotyl in the tube. Exchange of gases between the atmosphere and the thin layer of solution around the hypocotyl was negligible, especially when the hypocotyl had grown in diameter virtually to seal the glass tube.

The aerating gas entered at the bottom of the culture vessel through a narrow-bore capillary tube (*C*), bubbled through the nutrient solution into the gas space between the surface of the solution and the bottom of the stopper and through the outlet tube (*D*). The effluent gases could be collected for analysis

by the usual methods. No leakage could occur through the glass tube support if the bottom of the tube was always below the level of the solution and if no bubbles of gas escaped through the tube. The constant level siphon (*F*) guarded against the first contingency, and the latter possibility was avoided by directing the stream of gas bubbles away from the tubes. The root system also acted as a trap to prevent the entrance of bubbles of gas into the bottom of the supporting tube (*G*). Continuous solution flow was maintained from the solution reservoir by the constant level inlet siphon (*I*) and overflow siphon (*F*).

For soybean and tomato plants the roots were inserted in the glass tubes after germination and pushed through as the hypocotyl elongated. As the hypocotyls of some of the seedlings were shorter than the supporting glass tubes, it was found necessary, in order to thrust the root tips completely through the tubes, to etiolate the seedlings somewhat on the germination net before transfer to the glass tubes. A long hypocotyl permitted the roots to be exposed to the bulk of the solution so that a normal root growth could be obtained. For oats and other grains, the coleoptile could be inserted from below, exposing the roots to the bulk of the solution without the necessity of preliminary etiolation.

Preliminary experiments with control cultures grown by the usual technique showed that the manipulation required for this modification had no effect on the plant growth subsequent to the first few days after transplantation from the germination nets. The tubes must be of a sufficiently large bore to allow for normal increase in girth of the hypocotylar region.

The soybean plant was used for a major part of this work, further work being conducted with oat and tomato plants.

EXPERIMENTS WITH SOYBEANS

Soybean seeds were sterilized with 1:1000 $HgCl_2$, washed thoroughly with distilled water, and germinated on wet blotting paper in a large flat box covered with a pane of glass and black paper. They were then transferred to a germination net (6) over a pan of tap water. The pan was covered with another pan inverted to form a dark chamber for the etiolation of the seedlings. When the hypocotyls were of the proper length (5–7 cm.), six seedlings were transferred to each culture vessel as in figure 1. The part of the top above the cotyledons was exposed to the normal greenhouse atmosphere, and the roots were exposed to the bulk of the nutrient solution. The plants were grown in a substrate with an oxygen tension in equilibrium with air for 9 days after being transferred to the tubes.

Formula I of Shive and Robbins (6) was used as the basic solution. Ammonium sulfate was omitted, the cultures thus being supplied with only a nitrate as a source of nitrogen.

After 9 days of growth in air-saturated solution, each of the cultures was transferred to fresh solution and separately given four different oxygen treatments so as to provide cultures in which the roots of the plants were supplied with 0, 4, 8, and 16 p.p.m. of dissolved oxygen maintained throughout the treatment interval of 23 days. The plants were harvested at the end of this period.

After the first week of oxygen treatment, chlorosis developed in the leaves of the plants receiving 8 and 16 p.p.m. of oxygen in the substrate. The general yellowing of the leaves was more typical of nitrogen deficiency than of the type of iron deficiency characterized by green veins and chlorotic mesophyll. During the succeeding 3 days, which were of low light intensity, the plants recovered from the chlorosis and remained green. After 14 days of oxygen treatment the high-oxygen (8 and 16 p.p.m.) plants showed further symptoms of oxygen toxicity. The leaves became curled and crinkled, probably because of improper elongation of the veins. The leaves were also smaller than those of the plants in the 4 p.p.m. cultures.

These symptoms were noted in other experiments with soybeans which extended over 3 years and covered different seasons of the year. The most outstanding feature of these experiments is the production of symptoms of oxygen toxicity when soybean plants are grown at high levels of dissolved oxygen in the substrate. The symptoms are most severe during periods of bright sunlight.

Figure 2 shows the results of an experiment designed to demonstrate the nature of the chlorosis produced by a high oxygen tension in the substrate. All three cultures were given a continuous treatment of 8 p.p.m. of oxygen in a complete nutrient solution containing nitrates as the source of nitrogen. These plants became chlorotic after 1 week of treatment.

The culture on the left was given no forced aeration during the subsequent 28 days. Oxygen was obtained by diffusion from the air above the nutrient solution and also was supplied to the roots by the fresh nutrient solution entering from the solution reservoir. The oxygen content of such cultures fluctuates about a mean of 2–3 p.p.m. The root systems of this culture are less extensive than those in the aerated culture and are compacted in the upper portion of the vessel near the solution surface. Despite the poorer root growth, the culture is healthy and has completely recovered from the chlorosis developed during the initial week of high aeration.

The central culture (fig. 2) continued to receive the initial treatment for a further period of 28 days, during which the chlorotic symptoms increased in severity.

The culture on the right (fig. 2) was cured of the chlorosis which developed during the first week of the experimental interval by another course of treatment. These plants were given a nutrient solution containing ammonium sulfate as the source of nitrogen, in contrast to the previous treatment with

nitrate nitrogen.[2] Recovery was rapid, as is evidenced by the restoration of the green color of the leaves.

Thus the chlorosis could be corrected either by lowering the oxygen tension in the substrate or by adding ammonium sulfate to the nutrient solution.

The leaf distortion was most severe when only nitrate nitrogen was supplied in the substrate and was found even at 4 p.p.m. of oxygen when only nitrate nitrogen was present. When equimolar concentrations of ammonium and

FIG. 2 EFFECT OF OXYGEN IN THE SUBSTRATE UPON LEAF CHLOROSIS OF SOYBEANS

Plants of these three cultures showed leaf chlorosis produced by oxygen toxicity after vigorous aeration for 1 week in a solution with nitrate as the only source of nitrogen. Plants on left, continued for 28 days with NO_3 as the only source of nitrogen but without aeration, show complete recovery. Plants in center, continued as before, show serious oxygen toxicity. Plants on right, continued for 28 days with NH_4 as the sole source of nitrogen but with vigorous aeration, show complete recovery.

nitrate nitrogen were supplied, no chlorosis resulted even with the highest supply of dissolved oxygen (16 p.p.m.) but distortion of the leaves still occurred at the oxygen levels of 8 and 16 p.p.m. The leaf distortion, moreover, was

[2] The H ion concentration of solutions containing nitrogen in the form of nitrate only was maintained at approximately pH 5.0; that of the solution containing nitrogen in the form of ammonium was maintained at approximately pH 7.0. The pH values were chosen to ensure optimal rates of absorption of nitrogen in the forms under consideration.

independent of any pH changes in the nutrient solution, being found at both high (6.0–7.0) and low (3.5–4.0) pH levels.

The oxygen toxicity symptoms are aggravated by the presence of nitrate nitrogen. This may possibly be due to assimilation of the nitrate nitrogen, which provides a source of oxygen in addition to the atmospheric oxygen dissolved in the nutrient solution and absorbed by the plants. The use of ammonium salts as a source of nitrogen excludes this additional source of oxygen. The high light intensity of bright days probably aggravates the oxygen toxicity symptoms by increased photosynthetic activity and the pro-

FIG. 3. EFFECTS OF DIFFERENT OXYGEN LEVELS OF SUBSTRATES UPON SOYBEANS

Range of oxygen tensions in solution cultures, left to right: 0 p.p.m.; nonaerated, but solution surface exposed to air; 4 p.p.m.; 8 p.p.m.; 16 p.p.m. Roots of the culture on the left show severe symptoms of oxygen deficiency. Chlorotic plants of culture on the right show symptoms of oxygen toxicity.

duction of oxygen in the cells of the leaf, thus increasing the oxygen concentration in the plant.

Oxygen deficiency symptoms appear in the plants which received no oxygen, as shown in figure 3. In the oxygen-deficient cultures the roots are short, thick, and white and are clustered near the surface of the solution. They have relatively few branches. The position of the roots is attributed to failure to elongate properly under such extremely low oxygen tensions. As nitrogen gas is maintained in contact with the solution surface, there is no gradient of oxygen concentration from the top to the bottom of the solution. Such a gradient, however, does exist in static solutions with the supply of oxygen coming from the air above the solution and may account for the root growth only at the top of nonaerated solutions.

Since the proper supply of dissolved oxygen is necessary for good root development, and since root development is always reflected in top growth, the oxygen factor in the root environment must necessarily influence the growth of the entire plant. The influence of the oxygen tension of the substrate upon plant growth is shown in table 1, which gives the average green and dry weight production in a typical experiment with soybeans.

The green and dry weight data show that the amount of plant substance produced is directly related to the oxygen tension in the substrate. A secondary minimum in growth is often found at the higher oxygen tensions with soybean plants. Soybean plants make the best growth, from the standpoint of both external appearance and weight production, in solutions nearly saturated with oxygen at its partial pressure in the atmosphere.

TABLE 1

Green and dry weight production of soybean plants grown in substrates with oxygen tensions maintained at various levels

Average weight, in grams, per culture of six plants

DISSOLVED OXYGEN *p.p.m.*	0	4	8	16
Green weight:				
Top	63.2	81.9	86.4	97.1
Root	13.8	26.7	34.7	29.3
Total	77.0	108.6	121.1	126.4
Dry weight:				
Top	10.95	12.78	12.35	13.35
Root	0.82	1.35	1.72	1.60
Total	11.77	14.13	14.07	14.95

EXPERIMENTS WITH TOMATO AND OAT PLANTS

Tomato and oat plants were also used to study the influence of the oxygen concentration around the roots upon the growth of the plants. The technique already described for the soybean experiments was essentially the method used for these plants. The results, in general, were similar to those with soyb eans except that a higher oxygen tension was necessary for optimum growth of the oat and tomato plants.

The actual increase in green weight during the period of oxygen treatment was determined for both tomato and oat plants. The initial weights were obtained by weighing the plants in the rubber stopper supports and subtracting the apparatus weight when the plants were finally harvested.

The average increases in green weight of 6 tomato plants during 10 days of treatment at maintained oxygen levels in the nutrient solution were as follows: 16 p.p.m. O_2, 160 gm.; 8 p.p.m., 103 gm.; 4 p.p.m., 59 gm.; 0 p.p.m., 0 gm.

Prior to the initiation of the oxygen treatments the plants were grown at an oxygen level in the culture solution maintained at approximately 8 p.p.m. The plants were 77 days old at the time of harvest.

The data show clearly that tomato plants have a high oxygen requirement in comparison to soybeans. No evidence of oxygen toxicity was found during the 10 days of treatment at the highest maintained oxygen level. These data confirm previous findings (1) on the beneficial effects of aeration upon the growth of tomatoes in nutrient solution. The fact that the gain in weight at 16 p.p.m. of oxygen was much greater than that at 8 p.p.m. clearly indicates that in a given substrate the oxygen tension required for optimum development of this species may be considerably above that maintained at equilibrium with the oxygen of the air. It is significant also that at zero oxygen the plants failed to make any further gain in weight. In spite of the fact that these plants absorbed nitrate rapidly (3), the oxygen evolved in the process of nitrate reduction was not sufficient to maintain an effective metabolic status in the roots even for a brief time. In this respect the tomato plant differs radically from the soybean, in which the oxygen requirement is relatively low and the roots of which, with an adequate nitrate supply, can maintain for a considerable time, an active metabolic state during which the plant may gain substantially in total weight, even under conditions of a deficient external oxygen supply.

The experiments with oat plants were carried out in two series of corresponding cultures which received identical oxygen treatment. The plants of one series were grown without nitrogen during the period of treatment at the respective oxygen levels, while the plants of the second series were grown in complete nutrient solution. For 30 days prior to the initiation of the treatment the plants of both series were grown with the oxygen tension of the culture solution maintained at approximately 8 p.p.m. The plants were then transferred to corresponding solutions of the two series maintained at 0, 4, 8, and 16 p.p.m. of oxygen, respectively. The plants of the series supplied with nitrogen (NO_3-N) are designaed as +N plants, and those of the series without nitrogen are designated as −N plants. Weights were determined before and after the treatment interval, as in the experiments with tomato plants.

The numerical data representing the results obtained from the plants of the two series are presented graphically in figure 4. There is a marked increase in the production of green weight with increase in oxygen tension from 0 to 4 p.p.m. The increase above 4 p.p.m. of oxygen is slight in comparison to the increase over the range of 0–4 p.p.m., but the highest average increase was obtained with an oxygen tension at 16 p.p.m., indicating that the oxygen requirement for optimum growth of this plant is high. The steep slope of the graph between 0 and 4 p.p.m., with a sharp break occurring at 4 p.p.m., indicates that more than the external supply of available oxygen is involved in bringing about this effect. The explanation undoubtedly lies in the fact that, under conditions of a deficient external oxygen supply, the rates of nitrate absorption from the substrate and its reduction in the root tissues are high,

thus providing an internal source of atomic oxygen, which may be utilized in the metabolic processes to supplement the external oxygen supply (3, 5). With an adequate external oxygen supply the rates of both nitrate absorption and reduction are greatly retarded and the supply of atomic oxygen available for metabolic process is correspondingly reduced. This apparent transition phase from semianaerobic processes to aerobic processes may account for the steep slope of the upper graph of figure 4 at low oxygen levels and the leveling off of the graph as the external oxygen supply becomes adequate for the normal aerobic processes. This explanation is supported by the evidence of the lower graph of figure 4, which indicates that in the absence of a supply of nitrate in the substrate there is a straight line relationship between the yield and the oxygen tension of the nutrient substrate up to an oxygen concentration of 8 p.p.m. The oxygen supply at 4 p.p.m. is inadequate for growth in the absence of a supply of atomic oxygen from nitrate reduction. This explanation, how-

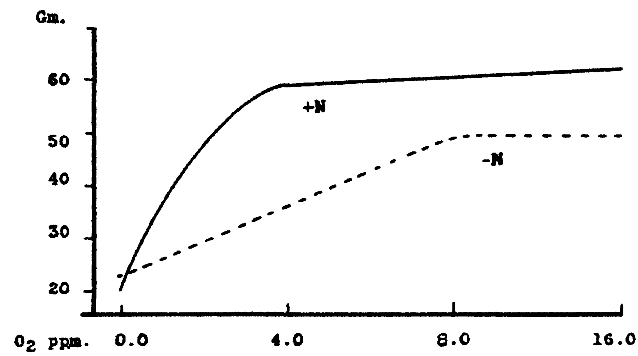

FIG. 4. AVERAGE GREEN WEIGHTS PER CULTURE OF SIX OAT PLANTS GROWN IN SOLUTION AT DIFFERENT O_2 LEVELS APPROXIMATELY MAINTAINED DURING AN EXPERIMENTAL INTERVAL OF 10 DAYS

The +N plants were grown in a complete nutrient solution with nitrate as the source of nitrogen. The −N plants received no nitrogen during the 10 days.

ever, is merely suggestive and should not be regarded as conclusive until confirmed by further experimental evidence along similar lines.

SUMMARY

Studies have been conducted with different plants to determine the influence of oxygen tension of the substrate upon the growth of plants in solution culture. A method is described for maintaining approximately a constant oxygen concentration in the nutrient solution. The method permits a quantitative study of the relationship of oxygen tension to plant growth.

Soybean plants show an approximate optimum oxygen requirement for growth in culture solution at an oxygen tension (6 p.p.m.) below the point of saturation at its partial pressure in the atmosphere. Below this optimum

the plants show oxygen-deficiency symptoms. Above the optimum, the soybean plant exhibits oxygen toxicity.

Tomato plants show a marked increase in growth with increase in oxygen supply, the maximum gain in green weight being obtained at the highest concentration (16 p.p.m.) of oxygen employed.

Oat plants also show the beneficial effects of an adequate oxygen supply by an increase in growth over that obtained in oxygen-deficient cultures. No oxygen toxicity was found with oat plants in these experiments, which covered a range of oxygen concentrations extended beyond that obtained in air-saturated solutions.

It is indicated that the optimum oxygen supply for maximum yield of certain agricultural species is not attained by the saturation of the nutrient substrate by air but is reached with a higher partial pressure of oxygen than is present in the atmosphere.

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BOOKS

Biological Symposia. Vol. IV. Edited by JAQUES CATTELL. The Jaques Cattell Press, Lancaster, Pa., 1941. Pp. 293. Price, $3.

This volume continues a practice of assembling in book form the symposia presented at recent meetings of the biological societies. It contains 19 papers dealing with population problems in protozoa; theoretical and practical aspects of polyploidy in crop plants; experimental control of development and differentiation; and the species concept. The subjects covered are diverse, but almost every worker in the agronomic field will find considerable material of interest and value in several of these papers.

Chromatographic Adsorption Analysis. By HAROLD H. STRAIN. Interscience Publishers, Inc., New York, 1942. Pp. 222, figs. 37. Price, $3.75.

A critical examination of and report on the columnar adsorption method for the detection, isolation, and purification of compounds which are not readily dealt with by any other means. As the name indicates, this procedure was originally applied to the purification of pigments, but is now being employed in many other fields. This is well exemplified in the 40 pages of bibliography that are appended. There are very few chemical laboratories which will not find some use to which the information contained in this book can be applied to advantage.

Investigations as to the Absorption and Accumulation of Inorganic Ions. By HENRIK LUNDEGARDH. Reprinted from the Annals of the Agricultural College of Sweden, Vol. 8, 1940. Pp. 233–404, figs. 36.

A report on experiments designed to elucidate the interaction of aerobic respiration of roots and the behavior of the surface of the protoplasm. The data support the author's electrochemical theory of the absorption and accumulation of ions in living cells and organs. An important publication in this field of research.

Laboratory Manual of Microchemistry. By I. B. JOHNS. Burgess Publishing Co., Minneapolis, 1941. Pp. 71, figs. 30. Price, $1.90.

A lithoprint presentation of methods in microanalysis employed in a graduate course in this subject at Iowa State College. In addition to methods for the estimation of the metals and the gaseous constituents of organic products, procedures are given for ascertaining the groupings of the organic elements; for the isolation, purification, and identification of the compounds of these elements; and for the determination of the physical constants of such compounds. A very useful reference book for workers in this field.

Laboratory Plant Physiology. Second edition. By BERNARD S. MEYER and DONALD B. ANDERSON. D. Van Nostrand Company, Inc., New York, 1941. Pp. 101, figs. 24. Price, $2.

This book contains suggestions for the carrying out of 177 experiments in plant physiology, beginning with those designed to clarify the basic concepts of molar solutions, acidity, buffer action, surface tension, surface energy, and adsorption, and concluding with those having to do with germination, plant growth, dormancy, and plant movements. Blank pages are interspersed between the printed pages for the convenience of the student. Detailed instructions for the preparation of special reagents are contained in the appendix. An excellent example of what a laboratory guide should be.

Soil Changes Associated with Loblolly Pine Succession on Abandoned Agricultural Land of the Piedmont Plateau. By THEODORE S. COILE. Bulletin 5 of the Duke University School of Forestry, 1941. Pp. 85, illus., 17. Price, $0.75.

As the author points out: "The object of the study was to measure and to evaluate the changes in soil characteristics associated with changes in natural vegetation on land once cultivated, and to determine the possible role of soil change as a causal factor in the development of successive stages of vegetation to the climax forest. Forest types involved in the successional series were loblolly pine and white oak, black oak, red oak." A very interesting study.

Soils and Fertilizers. By FIRMAN E. BEAR. John Wiley and Sons, Inc., New York, 1941. Pp. 352, illus. 58. Price, $3.50.

This is the third edition of the book by the same author which has previously been published under the title of *Soil Management.* The change in name was decided upon because of the ever-increasing importance of lime and fertilizer materials in maintaining and increasing the productivity of soils and because the book deals, in considerable part, with these materials and their uses. The book has been thoroughly revised, and some additional concepts have been introduced. The foreword deals specifically with soil erosion and its control. Though the book is intended primarily for student use in beginning courses in soils in agricultural colleges, it should prove very useful to those who, by experience or training, are in a position to profit from a modern statement of the problems of soil management and of methods for their solution.

A Symposium on Hydrobiology. Addresses given at an Institute held at the University of Wisconsin, September 4–6, 1940. The University of Wisconsin Press, Madison, 1941. Pp. 405. Price, $3.50.

This symposium was held under the joint auspices of the University of Wisconsin and its Alumni Research Foundation. The papers cover a wide range of topics in the field of aquatic biology, with particular reference to ponds, lakes, and streams. Among the subjects discussed were riparian rights, sediments, oxygen supply, bacteria, fungi and algae, fish production, sewage

disposal, and sanitation, as related to these inland waters. The topics of most general interest are those dealing with fish farming and the management and fertilization of ponds in connection therewith.

Technical Report Writing. By FRED H. RHODES. McGraw-Hill Book Company, Inc., New York, 1941. Pp. 125; figs. 7. Price, $1.50.

All graduate students, and many of their professors, would profit by a careful reading of this book. It deals with the characteristics of a good report; its organization; its form; styles, conventions, and correct usage; mathematical analysis of experimental errors; graphical presentation of data; statistical methods; dimensional analysis; and the symbols commonly employed. It also shows how a laboratory notebook should be kept so that not only will it serve as the basis for a report but it will also be available as evidence in litigation.

THE EDITORS

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THE HARDPAN AND THE CLAYPAN IN A SAN JOAQUIN SOIL

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The term "hardpan" connotes either the soil horizon or a layer of the parent material that is characterized by a hard stonelike consistency in which it differs from the other layers or horizons of the same profile. The usage of this term, however, has been rather loose, and the range of variability of individual characteristics of the hardpans, including their hardness, has been very wide. Some of the so-called hardpans are hard only when thoroughly dry but slake after wetting, whereas others are more or less permanently hard.

In this paper only the soil horizons or layers which are more or less permanently and, perhaps, irreversibly indurated will be considered as true hardpans.

Claypan is a dense and heavy soil horizon or a layer of the parent material which is characterized by a conspicuously large content of clay. It differs from hardpan especially in the lack of permanent induration. Usually, it is rather hard when dry and not uncommonly breaks into coarse, roughly prismatic clods, but becomes plastic, sticky, and impermeable after wetting. The percentage of clay in these pans usually is several times greater than that in the other horizons of the same soil.

Both the hardpan and the claypan range in thickness from a few inches to several feet and develop at a depth ranging from several inches to several feet from the surface of the soil.

In some soils both the hardpan and the claypan (the latter usually above the former) are present. The development of either pan, however, is not necessarily associated with the development of the other. Most of the claypan soils do not have the hardpan, and a great many hardpan soils do not have the claypan. The claypan soils are more common than the hardpan soils. The claypan soils develop especially on level land characterized by a somewhat impeded drainage, in depressions, on low terraces, and on broad undissected plateaus. As a general rule, the hardpan soils are more common in arid and subarid regions, whereas the claypan soils develop predominantly in rather humid regions. Many exceptions to this rule, however, can be mentioned. For example, ortstein is the iron hardpan that develops in the B horizon of the ground-water podzols in humid regions, whereas the well-developed claypan is not an unusual characteristic of various desert soils.

The San Joaquin and Madera soils of California are characterized by a conspicuous development of both the hardpan and the claypan. Nikiforoff points out (11) that the topmost part of their hardpan usually is the hardest and that

[1] Soil scientist and chemist respectively. The authors are indebted to S. B. Hendricks and G. T. Faust for helpful suggestions and criticisms and for assistance in the preparation and interpretation of the slides of the hardpan and the camera lucida drawing.

its upper boundary is abrupt, whereas the lower boundary is less distinct and cannot be determined precisely in most places. These hardpans are characterized by a bright red, dark red, or reddish brown color which is intense in the upper part of the pan and fades with depth. They have a weakly developed coarse platy structure which is somewhat better expressed near the surface of the pan but which vanishes in the middle and lower parts of it. The claypan which rests on the hardpan ranges in thickness from a fraction of an inch to about a foot. It is very sticky when wet and breaks into roughly prismatic clods after drying (fig. 1). It is dull reddish brown or brown, although bright red claypans are not uncommon.

FIG. 1. THE UPPER BOUNDARY OF THE HARDPAN IN THE SAN JOAQUIN SOIL. ABOVE THE HARDPAN IS THE CLAYPAN

Note the sharpness of the boundary between the two pans, the breaking of the claypan into prismatic clods, and the platy structure of the hardpan near its surface

The hardpan soils occupy large tracts throughout California and the other Western States. In the Central Valley of California alone they occupy several million acres of agricultural land, a large part of which is devoted to orchard culture. Because of its development so close to the surface of the soil and its impenetrability to the roots, the hardpan necessitates, as a prerequisite of successful farming, expensive operation, which naturally lowers the agricultural value of the soil.

This investigation has been made for elucidation of the general character of the pan formation. The data reported in this paper refer to the pans of the San Joaquin soil, which according to Shaw[2] represents "not only one of the

[2] Shaw, C. F. 1937 Some California soils and their relationships. University of California Press. (Mimeogr.).

extensively developed series in California, but also from the standpoint of soil science is of very great interest and importance." This particular soil has been chosen especially because its profile includes both the hardpan and the claypan, both of which usually are very well developed.

The samples used in this study were collected by R. C. Roberts in Section 35, T. 1 S., R. 9 E., in San Joaquin County, California. The profile of this particular soil is as follows:

0–20 inches. Light reddish-brown sandy clay loam. It is friable and mellow in a moist condition but hardens into a solid mass on drying. In the moist condition the entire horizon acquires a stronger red tint. Its texture near the surface is somewhat coarser than in the middle and lower parts. It has an acid reaction, ranging from pH 5.5 in the upper part to pH 6.1 in the lower part.

20–24 inches. The claypan. Dark brownish-red clay with an admixture of sand in the upper part. It has a compact and sticky consistency when wet and breaks on drying into roughly prismatic firm clods. It is nearly neutral in reaction, ranging from pH 6.9 near the surface of the claypan to pH 7.3 near the lower boundary. (Note a rather sharp change in soil reaction, from pH 6.1 to pH 6.9 at the upper boundary of the claypan.) It rests abruptly on the stonelike hardpan.

24–34 inches. The hardpan. Reddish brown to brown, firmly cemented, rocklike crust. It has a moderately developed medium to coarse platy structure. The pH throughout the hardpan ranges from 7.3 near its surface to 8.2 near its base.

34 inches and down. Light-brown structureless fine sandy loam. The pH is about 8.0. Slight rusty brown mottlings appear below the 50-inch level.

The upper friable horizon, the claypan, and the hardpan were divided for sampling according to the minor morphological characteristics each into three parts, upper, central, and lower, and two samples of the parent material were taken. Altogether 11 samples have been submitted for analyses.

RESULTS OF INVESTIGATION

Mechanical composition

Table 1 presents the data on the mechanical composition of the various horizons of the San Joaquin soil that are not cemented. The data indicate that the mechanical composition of the upper 20-inch layer of the soil is rather uniform throughout except for a noticeable increase of clay in the middle and lower parts at the expense of sand and silt. The composition of this material, however, is distinctly different from that of the loose material below the hardpan.

It should be borne in mind that the parent material of this soil is a more or less stratified water-laid drift. A certain difference in the composition of various layers of such a drift may be due, therefore, to the deposition of different materials rather than to the pedogenic alteration of originally uniform material. The conspicuous absence, in the upper layer, of gravel larger than 2 mm. in diameter, which is present throughout the profile from 20 inches downward, indicates that the upper layers consist of material different from that beneath. Another evidence of such a difference is the absence, in the upper layer, of large mica flakes, the presence of which in the material from 20 inches downward has been revealed by microscopic observations. This upper layer then must be

considered as a mechanical overlay of some sort not genetically related to the rest of the profile rather than the true soil horizon. Indeed, the material of this layer might have been somewhat modified after its deposition by the soil formation. The difference in composition between this material and that below the hardpan, however, cannot serve as a criterion for judging the character of such a modification and its influence upon the development of the lower soil horizons.

The data in table 1 demonstrate a relative uniformity in content of all materials larger than 0.25 mm. diameter in the claypan and the C horizon. This suggests that the claypan and more likely the hardpan have been developed from material similar to that of C.

The development of the claypan in which the percentage of clay is more than three times as great as in the parent material is very striking. Such an accumulation of clay raises the question: Where is this additional clay from?

TABLE 1

Mechanical composition of San Joaquin sandy loam

LABORATORY NUMBER	HORIZON	DEPTH	>2.0 MM	FINE GRAVEL, 2-1 MM.	COARSE SAND, 1-0.5 MM	MEDIUM SAND, 0.5-0.25 MM	FINE SAND, 0.25-0.1 MM	VERY FINE SAND, 0.1-0.05 MM	SILT, 0.05-0.002 MM	CLAY, <0.002 MM	ORGANIC MATTER
		inches	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
C-5321		0-7		4.2	14.5	10.7	19.7	15.4	27.0	7.8	0.6
C-5322		7-13		4.5	12.7	9.5	18.9	15.3	27.0	11.7	0.2
C-5323		13-20		5.0	12.7	9.4	18.7	15.1	26.2	12.5	0.2
C-5324	Cp*	20-22	1.1	3.4	9.5	6.9	14.1	13.0	22.3	30.3	0.4
C-5325	Cp	22-23½	0.7	3.3	7.3	5.0	11.4	11.4	19.5	41.4	0.6
C-5326	Cp	23½-24	1.0	3.8	8.1	5.7	13.1	12.7	21.4	34.5	0.5
C-5330	C	34-40	1.0	5.4	8.8	5.8	18.5	19.8	32.5	8.9	0.2
C-5331	C	50-76	0.8	3.9	6.7	5.1	20.3	22.0	37.0	4.7	0.1

* Cp = the claypan.

Has it been formed in place or carried downward from the upper soil horizons? Or is the claypan itself, perhaps, nothing more than a clayey layer of a stratified alluvial drift?

The morphological data, discussed in detail in another publication (11), suggest that in general the decomposition of certain material and the formation of clay in place have contributed more to the development of this claypan than the migration of clay from other horizons. The data in table 1 indicate an apparent loss of silt and of fine and very fine sands over that of the parent material. The claypan contains more than 10 per cent less silt, about 10 per cent less very fine sand, and 5 per cent less fine sand than the material below the hardpan. The increase of clay in the claypan is from 20 to 30 per cent (all in percentage of the whole soil). This gives reason to believe that the major portion of clay present in the claypan has been formed in place by the decomposition of the material composed of particles ranging in diameter from 0.25 to 0.002 mm. The absence of an apparent gain in content of the coarser fractions in-

dicates that the decomposition of silt and fine sand in the claypan has not been accompanied by the removal from it of the products of such a decomposition.

The data on mechanical composition of the hardpan material are not given in table 1. Because the hardpan is so strongly cemented by material not decomposed by the mechanical analysis treatment, the size distribution obtained depended upon the amount of crushing that was given the sample and hence had no significance.

It was thought, however, that the cement might be dissolved by chemical methods, leaving the coarser fractions, at least, largely intact. Accordingly, a sample of the upper part of the hardpan, C-5327, was crushed to pass a 2-mm. sieve, and a mechanical analysis was made. Another portion of this crushed material was subjected to alternate H_2S $(COOH)_2$ and 25 per cent Na_2CO_3 treatments. An analysis was run after each treatment to determine the amount

TABLE 2

Effect of chemical treatment on mechanical analysis of the San Joaquin hardpan

(Sample C-5327, depth 24-25½ inches)

	FINE GRAVEL, 2-1 MM.	COARSE SAND, 1-0.5 MM.	MEDIUM SAND, 0.5-0.25 MM.	FINE SAND, 0.25-0.1 MM.	VERY FINE SAND, 0.1-0.05 MM.	SILT, CLAY, AND DISSOLVED MATTER
Crushed hardpan material	14.4	19.3	9.3	17.9	14.3	24.5
Crushed hardpan after first Na_2CO_3 treatment	11.3	19.2	10.8	20.4	15.8	22.5
Same after H_2S-$(COOH)_2$ treatment	10.4	10.5	17.9	19.7	15.8	25.7
Same after second Na_2CO_3 treatment	4.8	11.7	8.8	18.9	19.5	36.3
Same after second H_2S-$(COOH)_2$ treatment	4.0	10.0	7.3	18.3	17.8	42.6
Same after third Na_2CO_3 treatment	4.0	9.8	7.0	18.3	16.0	44.9
Claypan from 22-23½-inch layer	3.3	7.3	5.0	11.4	11.4	60.9
C material from 34-40-inch layer	5.4	8.8	5.8	18.5	19.8	41.4

of breakdown of the cemented fragments. The results are presented in table 2, together with comparative data from the uncemented horizons above and below the hardpan. Apparently, the cement was completely dissolved by the last treatment, and the mechanical composition of the deconsolidated hardpan material seems to be intermediate between those of the claypan and the C horizon.

It will be noted that a prolonged first treatment for removal of cementing silica did not drastically change the mechanical composition of the crushed hardpan. The removal of cementing iron by the additional sulfide treatment did not materially affect the relatively large fragments 2-1 mm. in diameter but broke down about half the fragments in the 1-0.5 mm. fraction into fragments 0.5-0.25 mm. in diameter. Only the second treatment for removal of silica, repeated after the removal of iron, resulted in the disintegration of any considerable part of the fragments larger than 0.1 mm. in diameter and a sharp increase

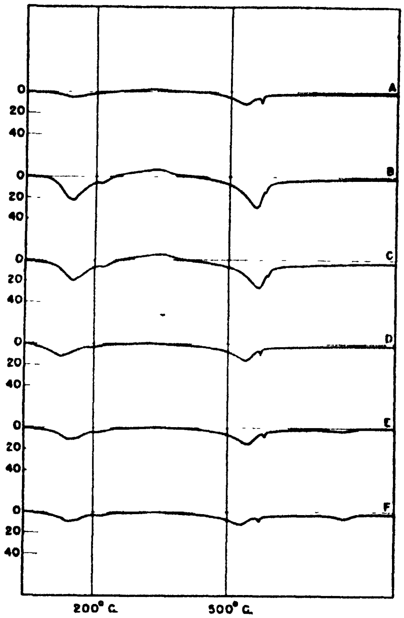

FIG. 2. DIFFERENTIAL THERMOANALYSIS CURVES OF DIFFERENT HORIZONS OF THE SAN JOAQUIN SOIL

A, sample C-5322; B, sample C-5325; C, sample C-5326, D, sample C-5327, E, sample C-5329; F, sample C-5330 The abscissas represent the temperature of the soil sample, and the ordinates, the temperature differences between the samples and the furnace The differential temperatures are expressed in microvolts as measured by a Pt- -20 per cent Pt Rh thermocouple. At 580°C , 10 microvolts correspond to 1°C

FIG. 3. CAMERA LUCIDA DRAWING OF A THIN SECTION OF THE SAN JOAQUIN HARDPAN

Q = quartz; SQ = secondary quartz; P = plagiocase; X = micaceous clay mineral. Magnification 750×. Drawn by G. T. Faust.

in content of the silt and clay and, to a lesser extent of very fine sand. This would seem to indicate the presence of both silica and iron oxide in the cementing material and, perhaps, their more or less layered deposition between and on the surface of larger primary particles which is distinctly seen under the microscope (fig. 4).

Although iron released by this treatment has not been determined quantitatively, it should be borne in mind that not all of it would come from the solution of the cement. If a clay mineral of the montmorillonite type containing considerable iron was present in this material, it would be decomposed by the treatment, yielding some iron that was not present as a free oxide in the cement.

In consideration of the genesis of the hardpan it is desirable to answer the question as to whether the hardpan is formed by cementation of the relatively unmodified parent material or whether this material was already altered before the cementation took place. Since the mechanical analysis threw no light on the question of the amount of clay present in the hardpan, it was decided to run thermal decomposition curves (fig. 2) to get an estimate of the quantity of clay present. The relative amounts of kaolin were determined in the whole soils by the method described by Hendricks and Alexander (6). Assuming a constant percentage of the 2-μ clay as being kaolin, and taking the percentage of clay in the uncemented horizons, C-5325 and C-5330, as reference points, the amounts of clay in the hardpan, C-5327 and C-5329, were calculated. Nineteen per cent clay is indicated for each of these two layers. On the same basis, an estimate of 28 per cent clay in claypan C-5326 is made, whereas the actual value by mechanical analysis is 34.5 per cent. Thus it is seen that, although not accurately determined, the clay percentage in the hardpan lies between that of the claypan and the C material. This lends support to the idea that cementation took place after a noticeable alteration of the original material by the clay formation.

Chemical composition

Table 3 presents the data on the chemical composition of the whole soil materials from various parts of the principal horizons of the San Joaquin soil, together with that of the fraction less than 2μ in three of the horizons.

The upper 20-inch layer of this soil, which is represented by sample C-5322, is more siliceous and contains less iron and aluminum than the other horizons. It is possible that some part of the sesquioxide content has been leached from this layer and a part deposited in the claypan. The extent of such leaching cannot be determined, however, because the original composition of this material is not known.

The claypan and the hardpan more likely are developed from material similar to that of the C horizon. The data in table 3 demonstrate the decrease in silica content of the claypan relative to the C material. This may be due in part to an actual loss of silica through its migration into the hardpan and in part to the accumulation in the claypan of the sesquioxides brought down from the overlying horizons. Since the reaction of the claypan is approximately neutral, some solution of silica may be expected. That some amount of silica migrates

into the hardpan and serves there as at least a part of the cement is indicated by the solution of the pan which has been described and discussed above.

A part of the increase in content of sesquioxides in the claypan apparently represents a true gain of iron oxide and alumina transported from the upper layer, whereas another part of it may represent a relative gain caused by migration of silica, lime, and soda from the claypan. It should be noted, however, that the percentage of lime in C, perhaps does not represent the original content in the parent material. A large part of this lime is in the form of carbonates. The carbonates in C likely represent a mixture of the original carbonates of the

TABLE 3

Chemical composition of the whole soil materials and of the clay fractions in the principal horizons of the San Joaquin soil*

Recalculated on 100 per cent basis of the material free of organic matter and combined water

LABORATORY NUMBER	HORIZON	DEPTH	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	P_2O_5
		inches	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
						Whole soil materials						
C-5322		7-13	73.71	14.62	3.39	2.43	0.66	2.24	2.21	0.62	0.04	0.21
C-5325	Cp†	22-23½	63.91	21.12	6.61	2.59	1.42	1.37	2.00	0.63	0.03	0.22
C-5326	Cp	23½-24	65.03	20.07	5.93	2.85	1.42	1.62	2.22	0.61	0.03	0.23
C-5327	Hp‡	24-24½	67.40	17.63	4.97	3.27	1.39	1.92	2.56	0.61	0.03	0.22
C-5329	Hp	26-34	66.45	18.32	5.00	3.60	1.48	1.77	2.58	0.57	0.04	0.20
C-5330	C	34-40	66.14	17.56	4.65	4.39	1.62	1.78	3.00	0.60	0.04	0.21
						Clay fractions						
C-5322		7-13	51.52	28.70	13.54	1.13	1.90	1.32	0.15	1.31		
C-5325	Cp	22-23½	52.19	29.01	12.84	1.26	2.61	0.60	0.29	1.22		
C-5330	C	34-40	51.62	25.34	11.82	4.49	3.91	1.23	0.53	1.06		

* $< 2\mu$.
† Cp = the claypan.
‡ Hp = the hardpan.

parent material and of the carbonates that have been leached from the upper horizons, including the claypan and the hardpan.

The data in table 3 also indicate certain changes of the parent material in the hardpan. Since the hardpan is virtually impermeable, there is little likelihood than any leaching of it or infiltration into and deposition in it took place after cementation of the pan. It is more likely, therefore, that the hardpan develops from material that already has been somewhat modified.

The increase of iron oxide in the hardpan is very small, in fact, hardly sufficient for the cementation and coloring of the pan. This suggests that most of the iron oxide that takes part in the cementation of the hardpan and gives to it its conspicuous color comes from the liberation of the combined iron and its oxidation and dehydration in place in the hardpan itself. Again, it is unlikely

that such processes take place in the pan already cemented. Perhaps they operate on the surface of the pan.

To obtain at least some idea of the character of the transformation of the parent material into the claypan, several recalculations of the data presented in tables 1 and 3 were made. The purposes of these calculations are, first, to compare the average composition of the coarse fractions (coarser than 2μ) in the original material and in the claypan and, second, to compare the distribution of various constituents between the fractions coarser and finer than 2μ in these soil horizons.[3] The results of these calculations are presented in table 4. These data demonstrate the summary effect of various reactions which took place in the parent material during its transformation into the claypan. The changes of

TABLE 4

Distribution of various constituents between the coarse and the fine fraction of the parent material and the claypan in the San Joaquin soil

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Parent material (C-5330):							
Percentage in the whole material	66 14	17 56	4 65	4 39	1 62	1 78	3 00
Percentage in the clay, < 2μ	51 62	25 34	11 82	4 49	3 91	1 23	0 53
Average percentage in the coarse fraction	67 57	16 79	3 94	4 38	1 40	1 84	3 24
Percentage of the total held in clay (rounded)	7	13	23	9	22	6	2
The claypan (C-5325):							
Percentage in the whole material	63 91	21 12	6 61	2 59	1 42	1 37	2 00
Percentage in the clay, < 2μ	52 19	29 01	12 84	1 26	2 61	0 60	0 29
Average percentage in the coarse fraction	72 30	15 45	2 16	3 53	0 57	1 92	3 22
Percentage of the total held in clay (rounded)	34	57	81	20	77	18	6

the original material in the claypan are due in part to the migration of certain constituents into or from this soil horizon and in part to their recombination in place. The data in table 3 indicate a possibility of leaching from the claypan

[3] The formula employed in these calculations is as follows:

$$x = \frac{100m - n.A}{100 - A}$$

in which m is the percentage of a given constituent in the whole material; n is the percentage of the same constituent in the fraction less than 2μ in diameter; A is the percentage of this fraction (less than 2μ in diameter) in the whole material; and x is the average percentage of a given constituent in the coarse fraction $(100 - A)$ of the soil. The percentage of the total amount of a given constituent in the whole soil, which is held in the <2-μ fraction is calculated as $\frac{n.A}{m} = y$.

of a part of the lime, soda, and perhaps of a small amount of silica and of the transfer into the claypan of a certain amount of sesquioxides.

The changes in the content of various constituents shown in table 3 indicate only apparent gains or losses of these constituents in the claypan. The true gains or losses could be learned only by calculating data obtained by analyses on a common basis represented by some constituent which is present in appreciable quantity and for which a relatively constant value in different soil horizons can be assumed. Since neither the immobility of the silica throughout the San Joaquin profile nor that of any of the sesquioxides can be assumed, such a basis is not available in this case and only a very general idea of the maximum possible gains or losses can be obtained. A relative uniformity in the content of coarse mechanical fractions and of nearly all minor elements in different horizons indicates that the translocation of some particular materials from one soil horizon into another was rather small. If it were possible to assume that an increase in content of alumina and iron oxide in the claypan relative to the C material (about 3.5 and 2 per cent respectively) was due only to the migration of these constituents from the upper layer, then these amounts of the migrant sesquioxides would suggest the maximum possible magnitude of the illuviation.

The data in table 1 indicate that the C material, sample C-5330, contains about 9 per cent of the clay $< 2\mu$, whereas the claypan, sample C-5325, contains about 41.5 per cent of such material, which constitutes an increase of more than fourfold. The data on morphology and mechanical and chemical compositions both indicate that a large part of such an increase in clay content is due to the formation of clay in place through the decomposition of the coarser material.

The data in table 4 demonstrate the general effect of such decomposition. The fraction of the C material $< 2\mu$ holds about 7 per cent of the total silica, about 13 per cent of the total alumina, and about 23 per cent of the total iron oxide, whereas the amounts of these constituents in the same fraction of the claypan make up about 34, 57, and 81 per cent of the totals respectively.

Again these figures do not represent precisely the true effect of decomposition of the original material. As has been pointed out, some alumina and iron oxide have been shifted into the claypan from the upper layer.

One may figure out that the clay $< 2\mu$ in 100 gm. of the C material contains 2.25 gm. of alumina and 1.05 gm. of iron oxide, whereas the same fraction in 100 gm. of the claypan material contains 12.01 gm. of alumina and 5.31 gm. of iron oxide. The increase in content of alumina and iron oxide in clay of the claypan is 9.76 gm. and 4.26 gm. respectively. Not more than about 3.5 gm. of alumina and 2 gm. of iron oxide (per 100 gm. of the whole material) have been brought into the claypan by illuviation, thus the minimum amounts of sesquioxides which should have been released in the claypan by decomposition of the coarse material and transferred into the clay fraction are about 6.26 gm. of alumina and 2.26 gm. of iron oxide per 100 gm. of the whole soil.

The release of free iron oxide and the deferrication of the coarse fraction are particularly effective. The average content of iron oxide in the coarse fraction

has dropped from slightly less than 4 per cent in the original material to slightly more than 2 per cent in the claypan. Another noteworthy point is the rather drastic decomposition of the magnesium minerals. The average content of magnesia has decreased from 1.40 per cent in the coarse fraction of the original material to only 0.57 per cent in the residue of this fraction in the claypan.

It is not definitely known whether the decomposition of the parent material in the claypan liberates much silica, alumina, and iron. The cementation of the hardpan by silica and iron oxides indicates, however, that some free silica and iron must have been present in the zone of cementation. Since the infiltration of any material into the already cemented hardpan is unlikely because of the impermeability of such a pan, the cementation perhaps takes place on the surface

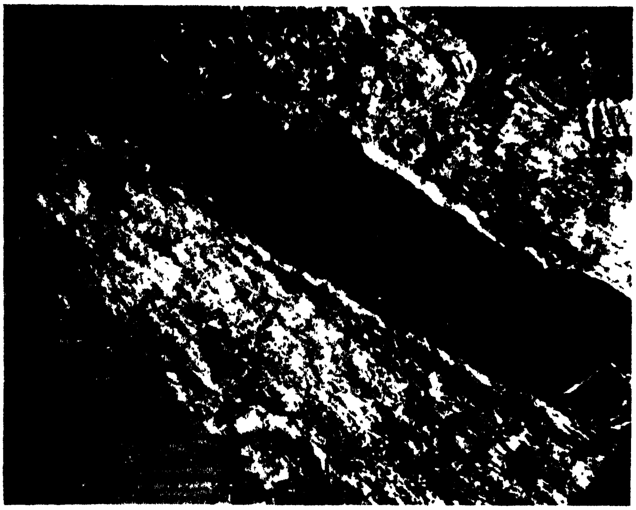

FIG. 4. LAYERED STRUCTURE OF THE CEMENTING MATERIAL IN THE SAN JOAQUIN HARDPAN

The central dark portion is a void, on either side of which is the cement. Whether this void was present in the original material or was formed by tearing out of a large grain during preparation of the thin section is not known. Crossed nicols. Magnification about 100×

of the hardpan only. It might be caused by an irreversible induration of the films formed by silica and free iron oxide on the surface, which was previously clogged, as well as on the surface of individual minerals. The induration of such films may bind together the grains of various minerals and paste them to the surface of the previously cemented layer.

In order to obtain information concerning the distribution and makeup of the cement of the hardpan, thin sections were made for petrographic examination. Figure 3 is a camera lucida drawing of features of the thin sections, and figures 4 to 7 are microphotographs. The two noteworthy points about the drawing are the secondary quartz growths and the layering of the micaceous clay minerals around the larger grains. This layering is also noted in the photographs.

The growth of secondary quartz is in harmony with the assumed deposition of silica in the hardpan as a cement. The layering of the clay minerals may be associated with deposition of the aforementioned films and a definite orientation of the clay minerals in such films.

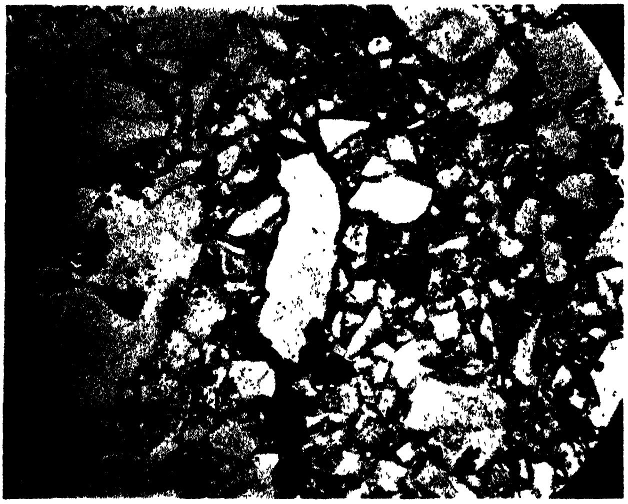

FIG. 5

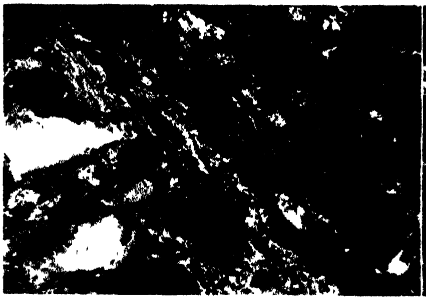

FIG 6

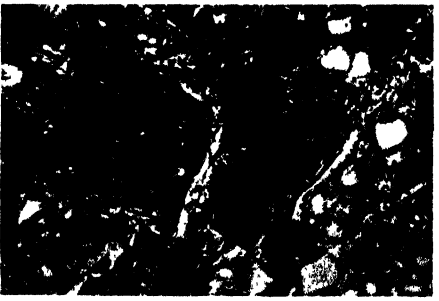

FIG 7

FIG. 5, 6, 7. PHOTOMICROGRAPHS OF THIN SECTION OF THE SAN JOAQUIN HARDPAN

Note layered cementing material between the larger crystals and the wavy extinction of the layered material around the large mineral grain. Magnification about 100×.

GENERAL DISCUSSION

Formation of the claypan usually is ascribed to the "illuviation" of the colloids into the claypan from the upper soil horizons. Brown et al. (2) conclude that their data indicate the "enrichment of the lower strata by illuviation," that "the translocation which occurred is essentially of colloid only," and that "the colloid as a whole is translocated from the surface downward by dispersion and illuviation. The transfer is from a point of lower to one of higher pH value."

This conclusion is in agreement with earlier views of Glinka. Describing podzolization and particularly the formation of heavy B horizons Glinka (4) says: "Essence of the podzolization is nothing more than an eluviation of the unstable sols of the unsaturated humus and under their protection of the fine mineral suspension from the upper soil horizons, and precipitation of such suspensions together with a small amount of humus in the B horizon." In this connection, Glinka also quotes from Hissink (8) that following the leaching of carbonates and certain exchangeable bases the soil gels pass into suspensions, sols, and true solution and that in such a condition the suspended particles of clay, the sols of iron oxide, and perhaps of alumina and silica are carried down by percolating water and accumulate in the lower soil horizons.

Gradually, the hypothesis about illuviation became well established in soil science, although its validity has not yet been proved. Smith and Norton (12) point out that it is more or less questionable that the high colloidal content in the thick plastic zone of certain soils can be attributed only to illuviation and suggest a probability of the formation of clay in place. The authors, however, do not present any data in support of their views.

Nikiforoff (10) has arrived at the conclusion that the claypans in certain desert soils are formed because of hydrolytic decomposition of certain minerals in place, and Brown and Drosdoff (3) assert that their investigation supports, to some degree, this view

Formation of the hardpan has also been attributed to a similar process of illuviation. Hilgard (7) says that the hardpan is formed by "the infiltration of cementing solutions into a pre-existing material, originally quite similar to that of the surface soil. Such solutions usually come from above, more rarely from below and are of various composition." Shaw upholds Hilgard's views. According to him the Madera hardpan, which is almost identical with the San Joaquin hardpan, "has been built up by precipitation of dissolved and suspended material washed down from the surface soil."

Glinka (4) thinks that the desert hardpans are formed by precipitation and accumulation of the cementing material from rising solutions, the lifting of which is caused by strong evaporation.

Nikiforoff (11) suggests that the formation of the San Joaquin and Madera hardpans may be due to an annual deposition of films of cementing material, including free silica and sesquioxides, which saturate a thin layer of soil and paste it to the surface of the previously indurated layer. The cementing oxides apparently are set free by the hydrolytic splitting of the aluminosilicates on the old surface of the hardpan. This process likely takes place during rainy winter seasons, whereas hardening of the fresh films may occur during the hot and dry summer and early fall months. The induration of the fresh films apparently is accompanied by the oxidation and dehydration of iron oxides, which give to the hardpan its conspicuous color.

The data presented in this paper indicate that silica and iron oxides are the principal constituents of the cement in the hardpan. A lack of appreciable accumulation of these constituents in the hardpan relative to the other soil

horizons suggests that most of these oxides, at least, must have been set free in place. The growth of secondary quartz and especially the layering of the cement that binds the coarse grains into the microconglomerate lend support to the idea that the hardpan develops because of induration of the films of cementing material deposited on the surface of individual minerals as well as on the old surface of the previously formed pan. If such is the case then it indicates that the hardpan is growing through the claypan by a gradual petrification of the claypan from below.

The boundary between the claypan and the hardpan is very sharp (fig. 1). As described in detail in another publication (11), perhaps this sharpness of the boundary between the two pans has been accentuated gradually and is itself an evidence of the upbuilding of the hardpan by induration of the additional films of cementing material on its surface.

Samples C-5326 and C-5327 represent two adjacent layers each one-half inch thick. The first sample represents the lowest part of the claypan and the second the uppermost part of the hardpan. The data in table 3 indicate that the upper sample (the claypan) contains about 2.5 per cent more alumina and about 1 per cent more iron oxide than the lower sample (the hardpan). The possible causes of an increase in content of the sesquioxides in the claypan have been described elsewhere. The average content of the sesquioxides in the hardpan, however, is approximately the same as in the parent material. If it is true that the hardpan is growing upward through the claypan, then the content of sesquioxides in the fresh films should be lowered before the induration of the film. Such a lowering of the sesquioxide concentration may be caused by an accumulation in the film of additional silica. One may calculate that an addition of about 13 gm. of silica per 100 gm. of the whole material would be necessary for such a dilution of the concentration of the sesquioxides and that such an addition of silica would bring its content in the fresh film to about 69 per cent. Again, this theoretical calculation suggests that silica which is set free by the formation of clay in the claypan is, perhaps, the principal ingredient of the cement in the hardpan.

The development of the San Joaquin hardpan has a certain connection with a peculiar microrelief described in detail in an earlier publication (11). Certain facts which are fully discussed in this publication indicate that the formation of such a microrelief antedated the formation of the hardpan. It has been suggested that the development of this microrelief might have been due to the hydrostatic pressure from underground water. According to this hypothesis, the San Joaquin and Madera hardpans develop under climatic conditions more or less similar to those which exist now and require between about 1,000 and 2,000 years to attain their average thickness. Prior to this time the climate apparently was somewhat cooler and more humid with much heavier snowfall in the high Sierras. The melting of this snow has caused a boggy condition on the plains adjacent to the base of the mountains. Perhaps, in these bogs the original nuclei of the hardpan were formed.

There is ample evidence of climatic changes during the Post-Pleistocene in-

terval. Matthes (9) describes a recent rebirth of the glaciers on the Sierra Nevada or a separate "little glacial age" and points out that "the present cirque-glaciers on the Sierra Nevada of California represent a new generation of ice bodies of late Post-Pleistocene origin, at most 4,000 years old." He quotes also from Antevs (1), who reinterpreted the Post-Pleistocene history of Owens Lake, and has arrived at the same conclusion regarding recent reglaciation of the Sierra Nevada. Hanson (5), who studied the delta of Bear River at the head of Portland Canal and the rate of its growth, has concluded that the glaciers at the head of the valley are only about 3,500 years old and represent a new generation of ice bodies born with the return of relatively cool and moist conditions during the last third of the Post-Pleistocene interval.

These facts indicate a marked change of climate from a relatively warm and dry one, which prevailed during the middle third of the Post-Pleistocene interval, to a somewhat cooler and more moist one of the earlier part of the last third of this interval. The reglaciation of the Sierra Nevada brought about by such a change in climatic conditions did not reach the scale of that which took place during the Pleistocene ice-age and was of a short duration.

The chronology of events (the hardpan is younger than the microrelief, which in turn is younger than the reglaciation of the high Sierras during the "little glacial age") indicates that the San Joaquin and Madera hardpans are of recent origin.

It is difficult to ascertain whether the claypan in these soils is older or younger than the hardpan. It is possible that formation of the embryonic hardpan began during the bog-stage of the region simultaneously with the development of the microrelief. Perhaps such an embryonic hardpan was different from the present one and was a kind of common "bog iron ore," or perhaps it was similar to the "immature" hardpans of the poorly drained Fresno soils. After the general decrease in supply of moisture from the mountains (the recess of the "little glacial age") and an improvement of drainage, followed by the general drying up of the land and lowering of the ground water table, this original hardpan very likely obstructed the free percolation of surface water and stimulated a more effective hydrolysis of the parent material above the clogged pan. This, perhaps, led to the development of the claypan above the embryonic hardpan, whereas the formation of clay began to supply the new cementing material which was and still is the cause of the growth of the hardpan.

SUMMARY

The profile of a San Joaquin soil having both hardpan and claypan is described. Mechanical, chemical, petrographic, and thermal analyses and field observations lead to the following conclusions regarding the formation of pans:

The clay in the claypan has formed largely by weathering, in place, of the silt and fine sand fractions with a possibility of a certain increase in content of colloidal material in this pan due to the transfer of such material from other horizons. The clay is not essentially different from that found in the parent material.

The hardpan was formed, subsequent to the profile development, by cementation of the

soil by iron oxide and silica. Apparently the cementing material was liberated by weathering at the points of cementation. When decemented, the hardpan has the same size distribution in the coarser fractions as the C material, which indicates that it has formed from material similar to that of the C horizon.

An estimate of the time required to form the hardpan is given, and its formation is correlated with the changes of climate during the later part of the Post-Pleistocene interval.

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THE USE OF THE MICROMETRIC AND OTHER METHODS FOR THE EVALUATION OF SOIL STRUCTURE[1]

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It is generally accepted that the structure of the soil exerts a controlling effect on air and moisture movements within the soil body. There has also been much importance attached to the influence of soil structure on plant growth, infiltration, soil erosion, tilth, and other soil properties.

Pore space in soils is directly related to soil structure. Every kind of soil structure has its own characteristic pore space. If we choose to think of soil structure as the arrangement of soil particles as they exist under natural conditions in the field, then the pore space becomes a characteristic of the structure itself. Natural structure, in this sense, cannot be adequately described without taking into consideration the sizes, numbers, and shapes of the various pores and without the use of some expression descriptive of the complete natural pattern of solid material and pore space. Thin sections of oriented samples of undisturbed soil were found to show excellently the natural soil-structure, pore-space pattern.

A method adapted from the Rosiwal method (10) for determining the volume-percentages of minerals in thin sections of rocks has been developed for expressing quantitatively the distribution of the soil pore space as revealed in thin sections of soil (19). The word "micrometric" is used in this paper to describe the adapted Rosiwal procedure because it defines the method briefly and descriptively.

The purpose of this investigation was to evaluate the accuracy of this newly adapted method for measuring the size distribution of pore space in soils by comparing it with other methods, especially a moisture-tension method perfected by Russell,[3] and to use this new method to study the structural characteristics which contribute to the apparent differences in the infiltration rates and other physical properties of virgin soils and soils that have been cultivated for many years.

HISTORICAL

The applicability and the accuracy of the Rosiwal method in the determination of the volume-percentages of minerals in rocks have been established by geolo-

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gists. In considering the problem from a mathematical viewpoint, Lincoln and Rietz (17) concluded that "if a plane is taken of sufficient extent so that any line in it will intercept lengths of minerals proportional to areas of sections, such plane will also make sections of minerals proportional to their volumes, and the sums of intercepted lengths will be proportional not only to area but also to volume." It was shown that the probable error could be reduced to 1 per cent by making a sufficient number of measurements.

Alling and Valentine (1) found that accurate volume-percentage measurements could be obtained by the linear intercept method in comparison with chemical methods and the planimeter method of estimating the volume of minerals in a rock. Another comparison between chemical analyses, specific gravity determinations, and the Rosiwal method was made by Johannsen and Stephenson (12). All of the results obtained were in good agreement. The theoretical relationships between areas and volumes have been developed by Johannsen (11).

The study of portland cement clinkers by microscopic methods has been reported by Ward (21). Quantitative measurements of the composition of clinkers were made with a Wentworth micrometer attached to the microscope stage. Each value reported was the average of five equally spaced traverses on each of five polished specimens. The method was found to be useful in evaluating the microscopic structure of portland cement clinkers.

There is less chance for error in applying the Rosiwal method to the volume-percentage of pore space in soils than to the volume-percentage of different minerals in rocks. In employing the Rosiwal method in a thin section analysis of rock (1) some of the factors entering into the accuracy of the method are: (*a*) uniformity of rock grain, (*b*) presence of appreciable foliation, (*c*) improper identification of minerals, (*d*) knowledge of the composition of minerals, (*e*) skill in manipulating instruments, (*f*) sufficient number of intercepts of areas, (*g*) proper choice of specific gravity of minerals, and (*h*) proper modification of norm calculation on basis of the true composition of minerals. About the only factors that will enter into a thin section analysis of the volume-percentages of pore space in soils are (*c*), (*e*), and (*f*). In the determination of pore spaces from minerals, (*c*) is virtually eliminated by the use of a gypsum accessory plate which causes the pore spaces to appear as a pink color under crossed Nicols, while the crystalline and noncrystalline materials exhibit their characteristic optical properties; (*e*) is reduced to a low value, since the only differentiation necessary is that between minerals and pores; and (*f*) is achieved by actually making a sufficient number of measurements.

METHODS AND RESULTS

Description of the microscopic method

To facilitate the microscopic work a method of microprojection was developed. It consisted of a system of mirrors which reflected the microscopic image on a flat surface containing a graduated scale which had been calibrated. This system when used with a 16-mm. objective of N.A. 0.25 and a 10× ocular gave a

magnification of 171× and made possible the rapid measurement of the intercepts of the pore spaces within the range of diameters of 0.0117 to 1.17 mm.

A petrographic microscope was used in producing the images, and since each Nicol prism wastes about 50 per cent of the light entering it (7), a carbon arc was employed for the source of light. Because it is necessary to rotate the stage in order to differentiate between minerals and pore spaces (19), a bumper device was designed so that the rotating stage could be easily and accurately returned to its original position at the completion of a determination. In order that the east-west and north-south locations of microscopic fields on the mechanical

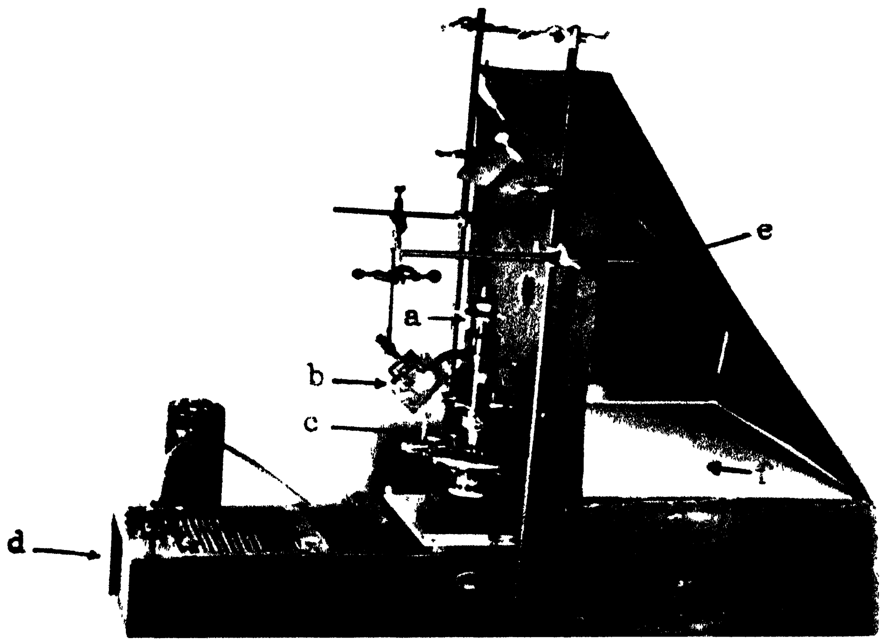

FIG. 1. MICROPROJECTION APPARATUS FOR MEASURING PORE SPACES IN THIN SECTIONS OF SOIL

(*a*) petrographic microscope with projection prism attached, (*b*) substage microscope lamp, (*c*) bumper device, (*d*) microprojector, (*e*) mirror, (*f*) graduated scale

stage could be read for orientation purposes while images were being projected in a dark room, a 10-watt substage microscope lamp was attached by clamps to the ringstands supporting the mirror. The illumination of the microscope lamp was sufficient for reading the position of a thin section, yet the light produced did not hamper the projection of the images. This apparatus is shown in figure 1.

Use of the micrometric method in comparing the structure of virgin and cultivated soils

In order to evaluate better the structural differences between a virgin and a cultivated surface horizon of Marshall silt loam, thin sections (13, 15) were prepared from undisturbed soil samples. The samples were taken approximately

6 miles south of Cherokee, Iowa, where it was possible to obtain samples representing these two conditions existing within a few feet of each other. The cropping history for approximately the last 50 years for the cultivated land has consisted mainly of corn and oats with an occasional seeding of clover, whereas the virgin soil has never been broken by the plow. Since the topography of the area sampled is essentially flat, it probably can be assumed that under both conditions the minimum amount of erosion has taken place. One thin section for each of four samples for each horizon was made with bakelite and kollolith as the impregnating mediums (19).

TABLE 1

Differences in the volume-percentage pore space† between virgin and cultivated Marshall silt loam‡*

CYLINDER NUMBER	THIN SECTION NUMBER	n§	VOLUME PERCENTAGE PORE SPACE
			per cent
Virgin			
1	640	332	14 09
2	641	322	14 73
3	648	336	15 11
4	650	281	12 92
Mean			14 21
Cultivated			
1	647	272	7 50
2	649	219	7 43
3	651	372	5 91
4	652	384	7 41
Mean			7 06

* Percentage of total volume of the sample.
† 0.0117--1.17 mm. size range.
‡ Soil samples obtained near Cherokee, Iowa.
§ Number of microscopic fields measured.

The data obtained by the use of the micrometric method are presented in tables 1 and 2 and in figure 2. A 50 per cent reduction in the amount of pore space (0.0117-1.17 mm. size range) as a result of cultivation is shown by comparison with the pore space of the virgin soil (table 1). The frequency distribution of the pores measured shows that the virgin soil was more porous (as evidenced by the fewer microscopic fields in which no pores were found) and had a larger number of pores of all sizes than did the cultivated soil (table 2). Strikingly shown in the cultivated soil was the rapid decrease in the number of pores in the size range greater than 0.439 mm. compared with the relatively large number of pores present above that size in the virgin soil (table 2).

TABLE 2

Comparison of virgin and cultivated Marshall silt loam on the basis of the frequency distribution of pores obtained by the micrometric method*

MIDPOINT OF CLASS INTERVAL	VIRGIN					CULTIVATED				
	Thin section number				Mean	Thin section number				Mean
	640	641	648	650		647	649	651	652	
mm †	*F*‡	*F*‡	*F*‡	*F*‡		*F*‡	*F*‡	*F*‡	*F*‡	
0§	82	43	45	47	53.50	59	61	90	75	71.25
0.029	257	453	491	325	381.50	299	231	399	447	344.00
0.088	77	93	100	57	81.75	64	29	34	60	46.75
0.146	35	31	40	29	33.75	18	17	20	19	18.50
0 205	18	28	31	20	24.25	9	9	5	18	10.25
0.263	14	7	17	19	14.25	5	6	6	11	7.00
0.322	7	9	9	8	8.25	4	5	6	3	4.50
0.380	11	3	7	3	6.00	2	4	2	3	2.75
0.439	5	5	5	2	4.25	2	4	4	6	4.00
0.497	3	1	1	2	1.75	1	0	0	0	0.25
0.556	1	3	3	1	2.00	0	0	2	0	0.50
0.614	4	3	2	0	2.25	2	1	0	0	0.75
0.673	2	2	1	1	1.50	0	0	0	0	0.00
0.731	0	2	3	1	1.50	0	0	1	0	0 25
0.790	3	0	0	1	1 00	0	0	1	0	0.25
0 848	1	1	1	1	1.00	0	0	0	1	0.25
0.907	2	1	1	0	1 00	0	0	0	1	0.25
0 965	1	2	0	0	0 75	0	0	0	0	0 00
1 024	0	0	0	1	0.25	0	0	0	0	0.00
1.082	0	0	0	2	0.50	0	0	0	0	0.60
1.141	6	5	4	3	4 50	0	0	1	0	0.25
Number of fields	332	322	336	281	317.8	272	219	372	384	311 7

* Soil samples obtained near Cherokee, Iowa.
† Pore diameters.
‡ Frequency.
§ Represents microscopic fields where no pore spaces were found.

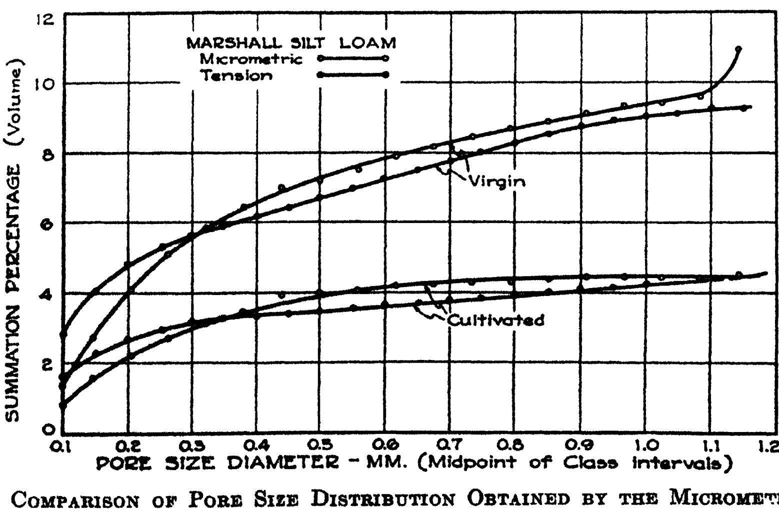

FIG. 2. COMPARISON OF PORE SIZE DISTRIBUTION OBTAINED BY THE MICROMETRIC AND TENSION METHODS

Comparison of the micrometric analysis with other methods

Specific gravity volume-weight method. Once it is apparent that differences in pore spaces in thin sections of soils can be measured micrometrically, the question naturally arises: How nearly comparable are such data to those obtained by other methods? Because the structure of a soil is commonly studied by determining the total, capillary, and noncapillary pore space by calculation from specific gravity, volume-weight, and moisture determinations (2), this was one of the methods selected for comparative purposes. Soil samples of Marshall silt loam for these measurements were obtained near Cherokee, Iowa.

A modified Coile (9) volume-weight sampling tube (3.8 cm. high) was used for obtaining undisturbed cores of soil samples for the determination of capillary and noncapillary porosity. Specific gravities of the soil samples were determined in the laboratory by the picnometer method, and the volume-weight and

TABLE 3

*Summary of specific gravity, volume-weight, porosity, volume-percentage pore space, and organic matter determinations**

HORIZON	POROSITY DETERMINATIONS†						ORGANIC MATTER§
	Specific gravity	Volume-weight	Total porosity	Capillary porosity	Non-capillary porosity	Volume-percentage pore space‡	
			per cent	per cent	per cent	per cent	per cent
Surface	2.60	1.07	58 85	54.01	4.84	11.0	5.31
A_3—14 inches	2.67	1.15	56.93	51.01	5.92	9.2	2.93
C—46 inches	2.72	1.24	54.60	51.75	2.85	6.3	0.26
Surface (virgin)	2.49	0.93	62.72	56.87	5.85	14.2	9.29
Surface (cultivated)	2.59	1.13	56.24	48.62	7.62	7.1	4.66

* Samples of Marshall silt loam soil obtained near Cherokee, Iowa.

† Means of two to six samples.

‡ Determinations by the micrometric method.

§ Means of triplicate determinations by the Walkley and Black method (20).

the total, capillary, and noncapillary porosity values were calculated according to the method of Baver (2).

There is no reason to expect the noncapillary porosity values, as shown in table 3, and those for volume-percentage pore space to be similar, since two different pore-size groups are dealt with by the two methods. It is quite probable that the lower pore size limit of the noncapillary pores would be greater in diameter than the 0.0117-mm. lower limit of diameter of pores determined by the micrometric method. At the very low pF that must exist when water is allowed to rise in a shallow column of soil, relatively large pores would hold water. In this experiment, soil cores 3.8 cm. high were used, in which capillary water would have an average pF of 0.28 based on the half height of 1.9 cm. The average size of pores holding water at this pF would be 1.5 mm. in diameter. It was expected, however, that results by the two methods would be in the same order of magnitude. The data in table 3 show that this was not the case.

Moisture-tension method. In recent years considerable work has been done in the investigation of the relationship between the moisture content of a soil and the pressure deficiency or tension with which that moisture is held. Because water movement must take place through the soil pores, the type, the rate, and the amount of movement are related to the properties affecting the nature of the pores. Among the kinds of water movement, two types are important (5): first, the movement in the larger pores through the action of gravity, or movement in a saturated soil, and, second, the movement in the smaller pores under the influence of capillary forces from surface to surface or in the small pores in the presence of numerous air-water interfaces, or movement in an unsaturated soil. The rate and the amount of movement of water are determined by the number, the size, and the configuration of the pores which are filled with moisture at the time flow takes place. The number and the size of the pores are largely determined by texture and degree of compaction, although granulation may reduce the capillary pore space content in favor of the noncapillary porosity (3).

Various methods (4, 6, 8, 16) have been devised to create the tension or suction pressure. Baver (4) is of the opinion that the shape of the pF-moisture curve is related to the permeability of a soil. The amount of water that is withdrawn from zero tension to that of the "flex point" of the curve appears to be closely associated with the rate of water movement through the column. This amount of water comes from the pores that have been drained and filled with air at tensions lower than that at the flex point. Baver classifies such pores as noncapillary.

Because of these recent investigations and because the energy concept of soil moisture has been applied to pore space determinations, it was decided to use Russell's[4] modification of Childs's (8) procedure to determine pore size distribution in samples of undisturbed soil.

Soil samples for porosity determinations by Russell's moisture-tension method were obtained as large clods when samples for thin section and volume-weight determinations were being taken from the area 6 miles south of Cherokee, Iowa. Since subsamples of these air-dry clods could not be taken without disturbing their natural field condition, the samples were wetted by spraying water on the soil surface with an atomizer. To reduce further any dispersing effect of the fine spray on the soil, cheesecloth was placed over the samples. Samples of the same diameter as the volume-weight samples but only 2 cm. high were taken with the volume-weight sampler.

Since noncapillary porosity is defined in terms of the size of pores that do not hold water tightly by capillary forces, it becomes obvious that the tension under which a soil is drained will affect the apparent amount of noncapillary pores. The moisture-tension curve was used to calculate the size distribution of pores in the soil. The calculations are based on the capillary-rise formula (14),

$$h = \frac{2T}{rDg}$$

[4] *Ibid.*

where h is the amount of tension expressed in centimeters of water with which the soil is in equilibrium, T is the surface tension, D the density of water, g the acceleration due to gravity, and r the radius of the capillary tube, which at 25°C. becomes,

$$d = \frac{2.94}{h}$$

where d is the diameter of the pore in millimeters. From the formula, it is possible to calculate the diameter of the pores emptied by any given tension. Only the range of pore sizes measured by the micrometric method (0.0117–1.17 mm.) was determined and used for comparison. These data are expressed graphically in figure 2.

DISCUSSION

In studying soil structure and its effect on other soil properties such as tilth, air movements, and infiltration, it is thought that knowledge of the distribution of pore spaces is as important as knowledge of the total amount. Moisture movements in natural soils, and especially under saturated conditions by gravitational forces, are considered (5) to be influenced by the amount and continuity of noncapillary pores in conjunction with other factors. The size of the pore has been said to be of utmost importance in the permeability of the soil for air (5). It is obvious, therefore, that some method is needed which would characterize more specifically the pores included in the arbitrarily designated capillary and noncapillary pore space groups. The commonly employed specific gravity volume-weight method provides information with regard only to the total porosity of a soil. Capillary pore space is often determined by placing a core of undisturbed soil on filter paper and allowing it to saturate capillarily with water. If the volume of water capillarily absorbed is considered to represent the volume of the capillary porosity of the sample, noncapillary porosity can be expressed as the difference between this value and total porosity. These values for capillary and noncapillary porosity, however, do not represent absolute constants. Neither do they express the nature, continuity, orientation, and distribution of pores in the noncapillary range nor their sizes, volumes, and shapes. Variations in the size distribution of either capillary or noncapillary pores may not be shown by the total amounts of capillary and noncapillary pore spaces separated at some arbitrary point. There are many possible pore size distributions that would yield the same total capillary and noncapillary pore spaces. Even though soils may have the same total porosity as revealed by the specific gravity volume-weight method, they may have marked differences in the distribution of pores. It is possible to define various grades of soil structure by the ratio of the total volume of pores of a certain size class either to the total porosity of the soil, or to the total amount of pore space represented by the noncapillary pores.

It has been shown (19) that when large sampling intervals (3 by 3 mm.) were

used, there was greater variability between individual sampling cylinders than between thin sections from the same cylinder. This variability was substantially reduced, however, by employing the smallest sampling interval (1 by 2 mm.) possible without the overlapping of microscopic fields (tables 1 and 2). The amount of work involved is not so great as to preclude use of the method as a means of characterizing structure in soil profiles. From 15 minutes to 1 hour was required to measure the pore spaces in a thin section of soil, depending on the size of the thin section, the number of pore spaces present, and the number of minerals which had to be distinguished from the pore spaces. The size of sampling interval is determined by the degree of accuracy desired. Differences in pore space between samples can be ascertained by the measurement of 50 to 100 microscopic fields per thin section on relatively few thin sections from each sample. Finer differences can be obtained by the micrometric analysis of more fields per section.

Because of the relation of pore space to soil infiltration rates, the micrometric method of appraising natural pore space was used to measure the difference in structure of Marshall silt loam surface soil from a long-cultivated field and from an adjacent area of unbroken prairie (table 1). For the sizes of the pores measured (0.0117–1.7 mm.), the cultivated area was found to have 7.06 per cent pore space as against 14.21 per cent for the uncultivated land. These differences make readily apparent the deterioration of structure from continued tillage and help explain the reduction in the infiltration rate of the cultivated land.

The similarity between the data obtained by the micrometric and the tension methods for the pore size range measured is apparent from the curves in figure 2. Because the micrometric method yielded a greater total pore space for the larger-sized pores than did the tension method, it appears that the tension method measured effective rather than actual pore space. It probably can be assumed that at each tension applied, not all the moisture was removed from those pores that calculations employing the capillary-rise formula indicated should be emptied by that tension. It would seem that not all the water is free to move and that some is held by forces other than surface tension. This probably increases the effective size of the soil particles, which would decrease the amount and size of the pore spaces. Thus, noncapillary pores may become of capillary dimensions and capillary pores may be completely closed to water movement. It is also likely that the pore space is actually reduced by swelling when the soil becomes wet. This hydration of soil particles, and especially of the soil colloids, has been shown by Lutz (18) to decrease the permeability of some soils. The fact that the pore spaces in the dry and in the wetted soils tended to approach the same total volume in the larger pore sizes (fig. 2) indicates that the effect of swelling was less pronounced in the larger pores. This is to be expected since the total volume of water film on the enclosing boundaries of a relatively few large pores will not be so great proportionately as that for numerous small pores. The frequency distribution of the number of pores of various sizes in table 2 shows that there is a greater number of the smaller-sized pores than of the larger.

For the pores smaller than 0.35 mm. in diameter as shown by the curves in figure 2, it is noted that as the size of the pores decreased, the difference between the two methods increased. Since the smallest pore size measured (range of the 0.1-mm. size interval, 0.075–0.125 mm.) is well above the resolving power and limits of error of measurement by a petrographic microscope (7), any error attributable to the instrument can be considered negligible. It is thought that the difference noted in the data obtained by the two methods may be attributed to the swelling and hydration of the soil. Thus, the larger pores became smaller, which would cause an increase in the numbers and aggregate volumes of the smaller pore sizes. This is shown for both the virgin and the cultivated soils, where there were more small pores (< 0.35 mm.) present in the wetted (as determined by the tension method) than in the air-dry condition of the soil (as determined by the micrometric method). There was also a greater total amount of small-sized pores (< 0.35 mm.) in the virgin than in the cultivated soil. A greater percentage of the total pore space, however, was found in the pores of small size in the cultivated than in the virgin soil.

Since nonpolar inert materials are used in impregnating the soils for thin section study, it may be assumed that a micrometric analysis measures the actual pore sizes existing in an air-dry undisturbed state. The fact that the pore space measured by the two methods (fig. 2) did not vary appreciably may be taken as evidence that thin sections of soil represent unmodified soil structure. For the reasons already given, it seems possible that differences between the actual (dry soil) and the effective (wetted soil) pore sizes can be measured by employing the two methods. This measure should also indicate the amount of swelling of a soil resulting from wetting. It is not known whether in the comparison of the two methods any significance can be attached to the point at which the curves cross. It is not believed that this point will always be at approximately the position shown in figure 2, since it probably varies with soil type, management, and other factors.

Since most of the soils of agricultural importance exist for a greater length of time in the unsaturated than in the saturated moisture condition and many of the surface soils for shorter periods of time are in an air-dry state, an analysis of soil structure in both the wet and the dry state should be of agricultural significance. It is now generally considered that the structural condition of the surface soil prior to a rain will determine to a large extent the amount of water infiltrating into the soil. A good idea of this condition can be obtained from a micrometric analysis of thin sections of soil in conjunction with methods which attempt to measure the structural stability. Whereas the ordinary method of aggregate analysis makes it possible to postulate the optimum size of granule for the most beneficial aeration and infiltration conditions in soils as well as structural stability, it is possible to observe microscopically in thin sections the actual optimum pore space arrangement of aggregates and pore space patterns. Moreover, the distance between aggregates of different sizes in their natural structural condition can be measured.

Since it is generally agreed that the larger-sized pores (or the arbitrarily desig-

nated noncapillary pores) are more significant in affecting the infiltration rate of water (under the influence of gravitational forces) than the smaller-sized pores (or capillary pores), measuring the larger pores in thin sections should give quantitative data which would be helpful in describing and interpreting the porosity of soils. By measuring only the larger pores, the operation of micrometric analysis could be speeded up, increasing the applicability and usefulness of this method in studying soil structure. A microscopic set-up of lower magnification would also enable the measurement of the relatively few large pores found in thin sections which at the higher magnifications are too large to be included.

The division of pore sizes into two groups such as capillary and noncapillary is useful in denoting pores that are filled with water and those that are not, but unless specified conditions have been agreed upon, the results obtained by one method will not agree with those of another obtained under slightly different conditions. It is believed that the micrometric and tension methods give a more accurate picture of the pore space relationship of the larger-sized pores in soils than can be obtained by calculation from specific gravity volume-weight and moisture determinations. If some moisture condition, such as the moisture equivalent, were used as the dividing point between capillary and noncapillary pores, then results from various methods would be comparable. Methods which employ the energy concept of moisture movement in soils appear to be the most promising. Since these values can be interpreted also in terms of diameters and of volumes of pores, no difficulty is experienced in comparing these data with those obtained when the micrometric method is employed. The micrometric analysis provides not only quantitative data regarding the sizes and distribution of pore spaces in samples of natural soil structure but also qualitative information of the shapes of pores in addition to the foregoing soil properties which are useful in the interpretation of the data. Whether or not the pores are continuous in nature is believed to be another factor influencing infiltration and other soil properties. Some idea of the extent of this property may be had from a thin-section study of a soil. These thin sections may be compared with those of other horizons in the profile or with other profiles.

An advantage of the micrometric procedure is that it allows actual observation of the numbers, sizes, shapes, volumes, and distributions of the larger-sized pores. The method enables the qualitative estimation of natural pore space in samples of undisturbed soil, a measurement necessary for the correct appraisal of the relationship between other natural phenomena and soil pore space. The results of the sampling studies show that a quantitative expression of pore spaces of sizes usually considered of noncapillary dimensions can be obtained by a micrometric analysis.

The micrometric method is another tool or method for studying the structural relationships of soils. Combined with soil moisture studies, it should provide additional means for the interpretation and understanding of natural soil phenomena. The volume-percentage pore space values are numerical expressions of the variable soil characteristic of natural pore space which affects permeability, tilth, air movements, and other soil factors.

SUMMARY

A micrometric method employing an adaptation of the Rosiwal technique for the volume-percentages of mineral grains in thin sections of rocks was applied to the measurement of pore spaces in thin sections of soil. Projection of the microscopic images on a graduated scale facilitated the measurement of the pore spaces.

The micrometric method of determining pore space was compared with a moisture-tension method. The moisture-tension method yielded pore space values comparable to those obtained by the micrometric method for a cultivated and a virgin soil.

The relationship of the natural structure of air-dried soils to wetted soils was shown. It appears that on wetting, the size of the pores was reduced by the swelling of the soil and that this swelling effect was least pronounced in the larger pores.

The pore space relationships of a cultivated and a virgin surface soil horizon of Marshall silt loam soil were studied. The results showed that for the range (0.0117–1.17 mm. diameter) of pore sizes measured, the virgin soil had twice the volume of pores and a higher percentage of large pores than did the cultivated soil.

An advantage of the microscopic study of soil pore space and structure in thin sections of undisturbed soil, is that not only quantitative but qualitative observations can be made of such properties as distribution, sizes, volume, and shapes of pores. The direct observation of the true structural pattern of the soil often yields information necessary for the correct appraisal of the relationships between soil structure and other natural phenomena such as infiltration capacity and soil pore space. Combined with soil moisture studies it provides additional means for the interpretation and understanding of natural soil processes.

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VOLUME CHANGE AND PORE SPACE OF SATURATED AND DRY SOIL CLODS IN RELATION TO DIFFERENT SOIL TYPES AND LAND UTILIZATION[1]

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An accurate determination of the pore space of soil with a natural structure is comparatively difficult. Nevertheless, the information obtained from such determinations is of great importance in studying the rate of infiltration of rainwater, in judging the susceptibility of soil to erosion, in estimating the major run offs, and in calculating the water-holding capacity of soil. In this connection, the change in pore space upon saturation with water is of prime concern. The practical methods[3] which are most frequently used involve the direct removal of cylindrical soil cores of different size. This proves to be valuable only when the soil is free from coarse stony inclusions and low in moisture, and when the compression required for sampling is at a minimum.

To eliminate these obstacles, Sideri[4] has proposed pore space measurements on irregularly shaped clods coated with a 4 per cent collodion solution. The method in its original description was found to have certain limitations when applied to local soil conditions. Thus, it was noticed that extremely small samples, 10–30 gm., could not be used successfully in the determination of volume by immersing the clod into a cylinder filled with mercury. Also, it was observed that the smaller the samples, the less accurate were the weighings under water. Applying collodion to the soil clods with a brush was found unsatisfactory because of the presence of numerous irregular pockets on the surface of the clod. Saturating the sample through a perforated brass plate is an extremely slow process, since only a small part of the angular soil clod is directly in contact with water.

To make the method more applicable to studying the pore space and related properties of undisturbed soil, it was found necessary to adopt the following procedure:

Soil clods of about 100 gm. are preserved in collodion as soon as they are collected in the field. In this condition, the clod can be transported to the laboratory without damage. In the laboratory, the sample undergoes the

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following treatments: (*a*) The clod is sawed in half with an ordinary hack saw. The old collodion is carefully scraped off, and the sample is scratched with the sharp point of a jackknife to assure a rough surface. (*b*) After the loose soil has been blown off, the two half samples are weighed on a torsion balance to one hundredth of a gram. (*c*) The clod at this point is ready for coating with collodion. Usually, one instantaneous dipping is sufficient to assure a fairly permeable and strong membrane. The samples, after being coated, are left to dry for 6 hours in the open air in order to ensure exclusion of ether or alcohol from the coated clod. (*d*) The coated clods are weighed on the same torsion balance on which the first prepared clods were weighed. (*e*) Next, the clods are saturated in about 70-ml. porcelain dishes filled with water to cover most of the clod. Beakers of 600-ml. capacity serve as suitable covers to prevent evaporation of water. The saturation point is not reached for 2 or 3 weeks for some compact subsurface soils, although for a majority of the surface samples complete saturation is attained within 2 or 3 days. (*f*) Weighing of the saturated clods under water can be conducted conveniently on the analytical balance by placing the aluminum bridge over the left pan. The bridge can safely support a 250-ml. beaker filled with water. To place the clod in the water, it must be attached to one end of a fine tag wire, which has been forced through the clod and bent around it part of the way. With the other end of wire it is hung on the hook of the left arm of the balance. The weight of wire under water is determined separately and is later subtracted from the weight of the clod under water. The weighings are made to one hundredth of a gram, and at the same time the temperature of the water is taken. (*g*) After the clod has been weighed under water it is left to dry partly or completely, depending on the nature of the pore space sought. (*h*) The dry volume of the clod is determined according to the Sideri method by immersion in a measured volume of mercury. (*i*) Computations are made according to the formulas suggested by Sideri,[5] $P_\Delta = \frac{d - d_\Delta}{d} \cdot 100$ for the total porosity of saturation, and $P = \frac{d - d_1}{d} \cdot 100$ for dry and partly saturated soil. In these formulas P_Δ is the changed total porosity of saturated soil; d, the specific weight of the solid phase; d_Δ the volume weight of saturated soil; P, the total porosity of dry soil; d_1, the volume weight of dry soil. Capillary pore space was obtained from equation $K_\Delta = \frac{\alpha}{V_\Delta} \cdot 100$, where Sideri[6] designates K_Δ as capillary porosity; α, as volume of absorbed water; and V_Δ, as volume of saturated soil.

Attempts were made to apply this improved clod-saturation method to a study of the pore space of nine different soil types, of which the principal one in each of the six series included, is described as follows:

[5] *Ibid.*
[6] *Ibid.*

Palouse silt loam, 0–20 inches, dull dark-brown or grayish-brown, friable heavy silt loam with a soft crumb structure. The B horizon, 21–30 inches, is tawny-brown, silty clay loam, columnar in structure and moderately compact.

Walla Walla very fine sandy loam, 0–8 inches, is brown, friable, noncalcareous very fine sandy loam, broken easily by hand into single grains. The B horizon, 9–20 inches, consists of light-brown, friable, noncalcareous very find sandy loam with a weak prismatic structure.

Athena silt loam, 0–16 inches, is dark-brown or dark grayish-brown, friable silt loam of platy structure. The B horizon, 17 28 inches, consists of yellowish-brown, moderately compact silty clay loam, massive in structure.

Waha stony loam, 0–2 inches, is dark brownish-gray stony loam, moderately high in organic matter, and with a soft crumb structure. The B horizon, 3–12 inches, consists of dark-brown or reddish-brown, compact, heavy-textured stony loam.

Couse silt loam, 0–12 inches, is brownish-gray, slightly granular silt loam. Organic matter content is variable, being highest when grass cover predominates over forest cover. The B horizon, 12–20 inches, consists of brownish-gray, slightly compact silt loam with small-crumb structure.

Helmer loam, 0–12 inches, is light yellowish-brown, single-grained loam, low in organic matter except for the surface 1 or 2 inches. The B horizon 13–20 inches, is light, brownish-gray loam or silt loam, slightly compact.

A study was included of the effect, on pore space, of land-use practices on each soil, such as growing sweet clover and alfalfa, range grasses and timber, summer fallowing, and stubble-mulch fallowing. Duplicate samples were taken in individual fields of the same soil type and also from widely separated fields to steady the variation in properties within each type. Preliminary data on a limited number of samples are reported in table 1.

Table 1 shows that the A horizon of Palouse silt loam runs consistently higher in pore space than horizon B, except in one case, a soil under sweet clover. The observed loose structure of the lower horizon in this area may account for this behavior. An outstanding feature of the soil from the sweet clover plots is that the pore spaces of dry and completely saturated soil from both the A and B horizons run appreciably lower than those of the soils under the other land-use practices.

From only limited data of widely separated locations, it is rather difficult to draw any definite conclusions in regard to the effect of stubble-mulch fallowing and stubble conserving on the pore space of the soil. The data show, however, that the pore space of moist Palouse silt loam in the A horizon is generally higher than that of the A horizon under clean-fallow practice. Total pore space in this soil was found greatest under a partly saturated condition of horizon A and under a completely saturated condition in horizon B. Capillary pore space is usually lower than or equal to the pore space of dry soil Volume change, ranging from 1.8 to 14.2 per cent, is small and is considered to be a minor factor in affecting the allied water-conducting properties of the soil.

The total pore space of Walla Walla very fine sandy loam, in contrast to that of Palouse silt loam, is usually greater in the lower horizon than in the upper. It follows the trend of the Palouse soil, however, in being highest in partly saturated soil. Perhaps on account of the coarser texture and more open structure resulting from the stubble-mulch fallowing, pore space differences for

TABLE 1

Total pore space, capillary pore space, and volume increase of certain soil types in relation to land utilization

SOIL	HORIZON	DEPTH	LAND UTILIZATION	TOTAL PORE SPACE OF DRY SOIL	TOTAL PORE SPACE OF PARTLY SATURATED SOIL	TOTAL PORE SPACE AT SATURATION POINT	CAPILLARY PORE SPACE	VOLUME INCREASE
		inches		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Palouse silt loam	A	2	Clean tillage	53.1	56.2	55.4	50.7	5.2
	A	7		48.1	54.3	52.3	48.6	9.4
	A	7		49.2	55.0	52.3	48.1	7.2
	B	24		45.4	46.8	49.9	46.5	9.7
	B	24		42.7	45.7	49.2	45.6	12.0
	A	2	Standing stubble	50.0	57.7	53.1	51.0	6.0
	A	2		51.7	58.0	54.2	51.1	6.1
	B	24		48.5	48.7	51.9	46.3	7.7
	B	24		46.9	47.3	49.6	46.3	4.3
	A	2	Stubble-mulch fallowing	55.7	59.6	56.2	51.9	2.0
	A	2		53.5	58.1	56.5	50.3	6.6
	A	2		52.3	54.7	53.8	48.9	5.7
	A	2		50.8	59.6	52.3	47.7	4.0
	B	24		46.5	46.4	49.0	47.5	6.2
	B	24		47.3	45.7	49.0	45.0	3.3
	A	2	Sweet clover	47.7	55.5	48.5	44.5	1.8
	A	2		46.5	57.7	50.8	44.3	8.6
	A	8		46.5	50.6	49.6	45.8	5.5
	B	24		50.0	52.5	53.8	48.1	7.0
	B	24		42.7	44.9	49.6	43.4	14.2
Walla Walla very fine sandy loam	A_1	4	Clean tillage	40.8	53.2	45.4	40.6	8.1
	A_1	4		43.5	51.7	50.0	43.7	13.5
	A_2	20		58.5	62.6	60.4	46.7	4.6
	A_2	20		59.6	63.8	63.1	57.7	8.5
	A_1	2	Standing stubble	53.9	55.1	54.6	50.8	1.0
	A_2	16		55.8	61.9	57.0	53.4	0.7
	A_1	4	Stubble-mulch fallowing	45.8	54.3	50.8	46.2	9.8
	A_1	4		44.2	54.3	48.5	45.9	7.7
	A_2	16		57.0	60.0	58.5	51.3	3.4
	A_2	16		50.4	56.2	55.0	51.4	13.0
Athena silt loam	A	2	Clean tillage	48.5	59.3	51.9	42.2	6.6
	A	2		45.0	56.6	55.0	43.6	9.0
	B	20		38.0	46.8	51.0	46.1	22.0
	A	2	Standing stubble	54.2	60.0	57.3	46.1	6.5
	A	2		51.9	56.2	54.5	46.5	5.0
	B	20		45.4	50.8	50.8	46.2	11.1
	A	2	Stubble-mulch fallowing	51.1	62.8	54.6	51.8	8.0
	A	2		48.5	62.8	52.7	46.6	9.3
	B	20		42.7	49.8	53.0	48.7	22.5

TABLE 1—*Concluded*

SOIL	HORIZON	DEPTH	LAND UTILIZATION	TOTAL PORE SPACE OF DRY SOIL	TOTAL PORE SPACE OF PARTLY SATURATED SOIL	TOTAL PORE SPACE AT SATURATION POINT	CAPILLARY PORE SPACE	VOLUME INCREASE
		inches		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Waha stony loam	A_1	4	Good range	43.1	52.8	51.2	47.9	14.0
	A_1	4		53.1	56.2	56.0	48.2	8.7
	A_2	8		46.5	52.5	53.0	46.8	12.4
	A_2	8		48.1	46.4	50.8	45.9	5.1
	A_1	4	Depleted range	40.8	47.1	45.8	41.0	9.2
	A_1	4		38.5	44.2	44.2	39.9	10.5
Waha loam	A_1	3	Good range	45.4	55.9	50.0	46.8	8.6
	A_2	8		45.4	51.7	50.0	46.1	7.9
Waha silt loam	A_1	3	Depleted range	48.9	51.3	49.6	46.3	1.6
	A_2	24		42.3	49.6	49.6	45.8	14 5
	A_2	18		45.0	49.2	49.2	45.8	8.7
Couse silt loam	A	3	Pea, fallow	44.2	48.1	48.1	43.2	7.0
	A	3		54.2	57.0	57.0	45.2	6.2
	B	20		40.0	51.3	45.4	41.2	10.4
Couse loam	A	2	Alfalfa	47.0	55.5	48.5	44.4	2.5
	A	2		47.7	56.0	48.8	44.8	2.2
	B	14		39.2	45.3	41.9	38.3	4.5
Helmer loam	A	3	Timber	71.5	74.0	71.9	65 5	0.6
	A	3		67.3	67.9	68.0	63.1	1.5
	B	16		68.5	68.0	68.1	59.8	0.0
	B	16		67.0	68.0	68.0	59.5	1 5

this series are not large. Capillary pore space and volume change are similar to those of the Palouse soil.

Athena silt loam, like the Palouse soil, shows more pore space in the A horizon than in the B. It has the greatest amount of pore space in the partly saturated condition. The B horizons of the two soils differ in capillary pore space and volume changes, which usually are higher in the Athena soil. This may have some bearing on reducing the permeability and infiltration properties of the Athena soil. The effect of rough stubble mulch fallowing and stubble-conserving practices on this soil is comparable with that on Palouse silt loam.

The amount of pore space in Waha stony loam seems to be controlled largely by the presence of stony material in the profile, since the variations in pore space of dry soil are very high. No significant differences in pore space can be observed between horizons A_1 and A_2. The effect of range depletion is shown by the smaller values for pore space in the A horizon as compared with the good-range plots.

Being classified as a compact, heavy-textured soil, the Waha soil types attain the largest pore space in partly saturated condition; yet they do not change appreciably upon complete saturation, which is not in exact agreement with the pore space values of the Palouse and Athena soils, also heavy-textured types. Some undisclosed factors must be responsible for the stabilization of pore space when this soil is in a partly saturated condition.

Waha loam and silt loam are shown in the table as minor soil types of Waha soil. They have more uniform pore space properties than the stony loam, and the effect of range depletion here is seen only when the soil is moist.

Couse silt loam, because of its slight compactness in the B horizon, shows little difference in pore space between the A and B horizons of the same plots when partly saturated. The B horizon of Couse loam, however, is definitely lower in pore space than the A horizon, which may be attributed to the effect of alfalfa on this plot, similar to that of sweet clover on Palouse silt loam. The general trend of larger pore space in partly saturated soil is identified here also. Capillary pore space and volume changes are in direct agreement with those of the Palouse soil.

The pore space of Helmer loam, a forest type of soil, was found to be as much as 20 per cent higher than that in the prairie types of soil. The apparent fluffy structure of the Helmer soil seems to be the factor that contributed to the increased total pore space. This is significant, because subsequently it was shown that the infiltration rates of this soil are extremely high. Only slight differences in total pore space are indicated between the A and B horizons, but the capillary pore space is definitely higher in the A horizon, which agrees with the description of the B horizon of Helmer soil as probably being a slightly compact silt loam. The change in volume of this soil upon wetting is practically negligible.

It may be concluded that the random figures obtained from each soil type under consideration show significant differences for the amount of pore space of soils from widely separated sampling points, but only slight difference when the samplings were close together.

The amount of total pore space in the surface soil generally was highest on partly saturated soil, considerably less on completely saturated soil, and lowest on dry soil. In subsurface soil, however, the total pore space was usually highest at the saturation point. The occurrence of maximum porosity of soil under partly saturated condition is the point which is not wholly understood. From the measurements of volumes of partly desiccated soil clods it was observed that the decreases in weights of clods were not followed by proportional decreases in volumes, but that disproportionately increased volumes were obtained instead. This seems suggestive of some transformation within the structural cells of soil.

The capillary pore space of the soils of the various series was consistently slightly lower than or equal to the total pore space of the dry soil. Exceptions occurred in the horizon B samples of the compact subsurface of the Athena soil and in horizon A_2 of the Waha soil, where in certain cases the capillary

pore space was greater than the total pore space of the dry soil. This deviation is probably due to the extreme compactness of these two soils.

Volume changes among the samples of the various soil types were found to vary within the range 0 to 22.5 per cent. The latter is significant because, according to Browning,[7] when the volume changes were greater than 20 per cent, the infiltration rates of the soil were found to be appreciably decreased.

Sideri's clod-saturation method as modified in this laboratory seems to provide an adequate means for successive measurements of total and capillary pore space, normal water retention, and swelling properties of soils. These properties are invaluable in determining the infiltration rates of the soil under field conditions.

SUMMARY

A modification of Sideri's clod-saturation methods has been worked out for the determination of pore space of soil under natural conditions in this region.

A limited number of data for pore space and volume changes of nine soil types were obtained by this modified method on soil samples taken from duplicate plots situated close together or far apart.

The data tend to show that for reliable results the study of pore space on heavy-textured soils of the same type must be conducted on samples obtained from closely adjoining areas, for significant differences in values may be obtained when the sampling areas are far apart.

The study of pore space at the different moisture contents employed in this work suggests the possibility of obtaining reliable information on soil-water relations, when control of a desirable soil structure is contemplated.

Different land-use practices were found to be effective in altering the original pore-space capacity on some soils.

[7] Browning, G. M. 1939 Volume change of soils in relation to their infiltration rates. *Proc. Soil Sci. Soc. Amer.* 4: 23–27.

INFILTRATION STUDIES IN THE PECOS RIVER WATERSHED, NEW MEXICO AND TEXAS

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THE WATERSHED PROBLEM

From its source in central New Mexico to its confluence with the Rio Grande, 525 miles to the south, the Pecos River watershed is used predominantly for grazing, and those lands adjoining the river valleys are intensively cultivated under irrigation. The grazing lands have been subjected to varying degrees of overuse that has caused depletion of the vegetal cover.

The only long-time solution to widespread overuse of natural resources is conservation through management. Watershed management, in broad terms, is a system of regulated use to ensure the yield of good-quality water and at the same time allow the maximum use of range and other agricultural resources. The condition of the land, the frequent damage by flood, and the rapid diminution of the capacity of storage reservoirs are indications of the fact that past use of soil and water resources has not been on a basis of sustained yield. Since grazing is the major use of lands in the Pecos basin, the main task in this area is to effect a system of range control that will allow rehabilitation of the depleted plant cover and thereafter maintain range lands in a condition of sustained productivity.

PURPOSE OF INFILTRATION STUDIES

As in all the major watersheds in southwestern United States, vegetation in the Pecos basin is more or less delicately adjusted to topography and climate. Grazing pressure has reduced forage production and in some places encouraged replacement of forage species by unpalatable herbs and shrubs. The change in vegetal cover has been partly the cause of, and certainly has been accompanied by, important changes in the rate of water intake of the soils. Organic matter, scarce enough in soils of semiarid areas under ordinary conditions, has been decreased by the replacement of grasses by weeds and shrubs. Plant litter on the soil surface, structure of the A horizon, and dispersion of the clay are all affected by the changes in vegetation.

As part of a flood control study, infiltration experiments were conducted in an attempt to evaluate these changes. The data obtained were used to project the effect of a change of vegetal cover in terms of a change in the rate of infiltration.

SOILS AND VEGETATION

Bounding the watershed on the north and nearly all along the western edge are ranges of mountains, rising in places to 12,000 feet elevation. In the mountain

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areas the soils are stony, shallow, dark in color, high in organic material, and show some profile development. These areas receive 20 or more inches of precipitation and are covered by coniferous forests.

In the central portion of the watershed ephemeral streams flowing east from the mountains have dissected a formerly extensive alluvial apron of coarse clastics, leaving a rolling plain underlain by limestone and red beds covered in places with pediment gravels, and with terrace deposits near the stream valleys. The soils of this central portion are characteristically shallow and calcareous, have textures varying from clay loam to clay, and show little profile development. The average annual precipitation varies from 14 to 18 inches. The soils may be classified as brown or reddish-brown soils. The vegetation is predominantly short grass of turf-forming variety, including blue grama (*Bouteloua gracilis*), galleta (*Hilaria jamesii*), and bluestem (*Agropyron smithii*). Improper use of these grassed plains has caused suppression of the desirable palatable grasses and has encouraged annual weeds, snakeweed, and rabbit brush.

In the southern portion of the watershed where the annual precipitation is 12 to 16 inches the soils are shallow and calcareous. The vegetation is desert grassland and desert shrub associations of which creosote bush (*Covillea tridentata*) and saltbush (*Atriplex* spp.) are characteristic. The soils of the area may be broadly classified as desert soils.

SELECTION OF PLOTS FOR INFILTRATION STUDIES

Since the Pecos River watershed comprises 37,000 square miles, large variations in soil characteristics and vegetal cover may be expected. The funds and the time available for infiltration studies allowed only a limited number of tests; therefore, 12 different combinations of soils and vegetation were selected for study. Each combination of soil type and vegetal cover was designated as a "stratum." It was the plan of this study to measure the effect of vegetal density on each stratum by sampling extremes of density. Plots were selected on each stratum to include areas of dense vegetation and areas of sparse or no vegetation. Since an important effect of a program of range management is an increase in vegetal density, this factor furnishes an index to the prospective value of a conservation program.

It must not be assumed that an increase in vegetal density necessarily is synonymous with an increase in forage production. For example, in a blue grama range, overgrazing may increase the ground density because continual trampling and cropping of the crown cover forces a change from an original bunch-grass type to more of a sod-forming type. But in this type of cover such overuse will reduce the plant vigor (6), decrease the volume growth of usable forage, and diminish the surface litter, which alone is a potent factor in keeping surface pores of the soil open and thus increasing infiltration. Again, overuse of a tobosa grass range may encourage replacement of tobosa by burro grass which, though having a higher density than the tobosa, produces less usable forage and actually decreases the infiltration rate. One set of experiments in this study showed that four plots of burro grass with 68 per cent average density had an

average infiltration rate of 0.50 inch an hour, while nearby tobosa plots on the same soil had an infiltration rate of 2.20 inches an hour, in spite of having a slightly lower density.

In the plots tested, bare or nearly bare areas were compared with areas in which the vegetation was in relatively good condition. Except in certain vegetal types, in which the initial effect is an artificial increase in density accompanied by lower plant vigor and volume growth, or where grazing has caused replacement of bunch grasses by less desirable turf grasses, density is one indication of range condition.

In the selection of plots, fenced areas were chosen within which no grazing was allowed. For example, plots were selected in a fenced graveyard, and other plots were chosen immediately outside the fence. The actual location of an individual plot was chosen more or less at random.

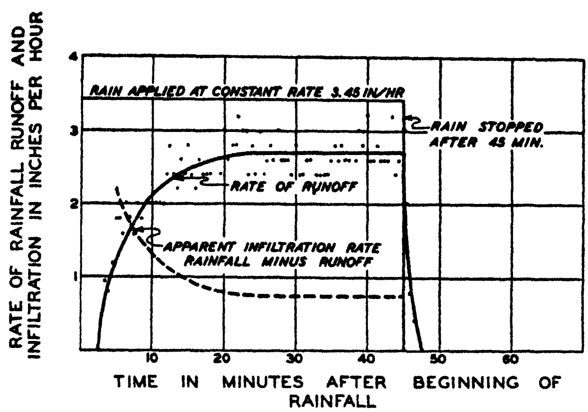

FIG. 1. TYPICAL INFILTRATION RUN, PECOS WATERSHED STUDY

Plot 4, run on wet soil April 10, 1940; soil, shallow, gravel sandy loam; vegetation, desert grassland, density 17 per cent; slope 9 per cent.

CONDUCT OF THE FIELD INVESTIGATION

The data summarized in this paper were obtained by the use of an artificial rain applicator developed by the Department of Agriculture. It employs the use of a 12- by 30-inch plot surrounded by thin galvanized metal plot borders, 6 inches high. The plot was covered by a canvas tent to keep the wind from blowing the raindrops. The machine, called the "North Fork" type, produces raindrops smaller than those of natural rain and gives a rate of infiltration somewhat greater than that under conditions of natural rainfall.

The intensity of water application was held constant during the run, and the average rate was determined by calibration runs before and after application of rainfall to the plot. For the calibration, the plot was covered by a metal pan that collected all water applied to the plot.

Runoff was collected in a can equipped with a hook gage for measuring the volume of water, and the time of each reading was recorded with a stop watch.

Readings were taken at half-minute intervals while the rate of runoff was changing, and at intervals of 1 to 5 minutes after the rate had become more or less constant. No test was run less than 50 minutes.

The vegetation on the plot was clipped to approximately 1 inch in height, but no natural litter was removed from the plot surface.

After each test was completed the data were plotted in the form of a graph, a typical example of which is presented in figure 1. A smooth curve was drawn through the points showing the instantaneous rate of runoff at a given time after the beginning of rainfall application. The apparent infiltration rate at any time was computed by subtracting the instantaneous rate of runoff from the corresponding rate of rainfall.

An initial "dry" run was made on the soil under conditions of field moisture. Twenty-four hours later, water was again applied to determine the infiltration rate for the soil at field moisture capacity.

Soil moisture samples were taken from within the wetted area outside the plot borders before both the dry and the wet run. A second wet sample was taken inside the plot after completion of the wet run. Soil profile samples for analysis were taken alongside each plot.

LABORATORY PROCEDURE

Mechanical analyses were made by the pipette method as outlined by Olmstead and others (9), except that the pretreatment was omitted. Instead of using sodium oxalate alone as a dispersing reagent, a mixture of sodium silicate and sodium oxalate was used. The dispersion ratio (percentage of dispersed clay) was determined by the procedure outlined by Volk (11), which is based on the 5-μ clay instead of the silt plus clay as determined by Middleton (8). The pH determination was made on a 1:2 soil-water suspension, by means of a glass electrode. Moisture equivalent was obtained by the method of Briggs and McLane (2). Organic matter content was determined by a modification of the Schollenberger rapid-titration method (10), as outlined by Allison (1). Moisture samples were collected in 16-ounce tin cans and dried in the oven at 110 C. for 40–48 hours.

BASIC DATA

Both a dry run and a wet run were made on each of 264 plots. Soil analyses were made of samples taken from 126 of the plots, and the statistical analysis employed the data obtained. For the investigation of the effect of vegetal density, composite curves were drawn using all the 264 plots.

In order to have comparable data, so far as initial soil-moisture conditions were concerned, only the wet runs were used for the comparisons that follow. The effect of initial soil moisture is discussed separately.

The final rate of infiltration of the 126 soil profiles analyzed varied from 0.05 to 5.64 inches an hour. The mean was 1.03 inches, and the median was 0.85 inch an hour.

Relation between final infiltration rate for wet run and vegetal density

The average figures presented for a given vegetation type were taken from plots having comparable soil profiles

VEGETATION	MEAN DENSITY	MEAN FINAL INFIL-TRATION RATE	NUMBER OF RUNS	RANGE IN DENSITY		RANGE IN FINAL INFILTRATION	
				Maxi-mum	Mini-mum	Maxi-mum	Mini-mum
	per cent	*in./hr.*		*per cent*	*per cen*	*in./hr.*	*in /hr.*
Grassland	4.8	0.81	11	8	Bare	1.48	0.12
	16.2	1.06	12	19	13	2.06	0.46
Grassland	Bare	0.75	3	1	Bare	1.16	0.44
	19.3	0.74	7	25	15	1 40	0.25
Desert-shrub	Bare	0.27	3	Bare	Bare	0 45	0.17
	27 2	1 96	6	58	8	3.33	0 28
Desert-shrub	Bare	0.27	3	Bare	Bare	0.45	0.17
	18.1	0.95	11	20	8	3.33	0.20
	37 2	1.87	4	58	25	2.78	1.60
Grassland	6.1	0.74	5	10	2	1.00	0.37
	20.4	0.87	5	28	13	1.14	0.55
	77.0	4 54	2	89	65	5.64	3.44
Woodland	54.2	4.07	4	80	33	7.17	1.70
	20.5	1.24	4	30	1	2.56	0.66
Desert-shrub	5.0	0.35	4	9	1	0.50	0.18
	16 3	0.53	5	28	12	1.03	0.45
	55.7	2.05	3	60	37	2.66	1.50
Desert-shrub (tobosa grass)	Bare	0.37	3	Bare	Bare	0.59	0 24
	64.3	2.24	3	70	53	4.20	0.61
	57.3	2 48	3	72	40	3.38	0.80
Desert-shrub (burro grass)	Bare	0 19	2	Bare	Bare	0.32	0.06
	68.0	0.50	4	70	62	1.42	0.14
Grassland (blue grama)	Bare	0.29	3	Bare	Bare	0 40	0.09
	63.3	0.68	3	75	45	1.29	0.29
Desert-shrub	Bare	0.38	3	Bare	Bare	0.40	0.05
	4.1	0.75	9	10	1	1.23	0.43
Desert-shrub	Bare	0.53	6	Bare	Bare	0 90	0.30
	5.7	0.96	6	12	2	1.65	0.40
Desert-shrub	2.2	0.24	4	3	1	0.56	0.20
	19.2	0.64	7	39	8	1.27	0.15
Grassland	13.7	1.11	3	27	5	1.44	0.48
	46.2	2.39	4	60	40	2.88	1.50
Woodland	6.8	0.85	2	12	2	1.33	0.37
	23.7	1.10	3	25	21	1.83	0.61
Woodland	13.0	0.44	2	19	7	0.51	0.36
	34.7	1.23	3	40	29	1.69	0.77

RESULTS OF THE INVESTIGATION

Effect of vegetal density

Table 1 shows that the vegetal density is one of the most important factors governing the infiltration rate. As the density of cover increases, so also does the rate of intake. For example, in desert-shrub type on a given soil, a series of plots having average densities of 0 (that is, bare plots), 18 and 37 per cent, had final infiltration values of 0.27, 0.95, and 1.87 inches an hour, respectively. Within each stratum the same relation was true in general.

An example of a composite curve of infiltration rate showing effect of vegetal density is presented in figure 2.

The effect of vegetal density in increasing infiltration rate may be attributed to a number of factors, the relative importance of which has not been evaluated. Vegetal cover tends to break the impact of raindrops on the soil surface. The

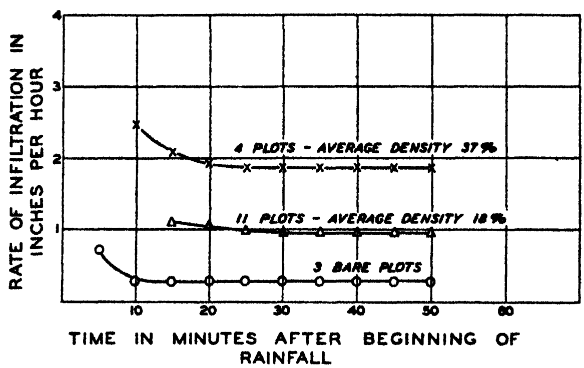

FIG. 2. TYPICAL COMPOSITE CURVES OF INFILTRATION RATE SHOWING EFFECT OF VEGETATIVE DENSITY

18 runs on wet soil; soil, deep clay loam—light clay; vegetation, desert shrub; vicinity of Roswell, New Mexico.

importance of sealing of surface pores by inwash of colloidal particles has been noted by Lowdermilk (7), and by Duley and Kelly (4). The vegetal density probably affects the organic matter in the soil, which has been shown by Free, Browning, and Musgrave (5) to be correlated with infiltration rate.

That this increase of infiltration rate with vegetal density is more than mere chance is shown by the results of a correlation analysis in which the data from 126 plots were used. The correlation coefficient was computed to be 0.46, whereas the value of r would be 0.23 at the 1 per cent level of significance.[2]

[2] $$r = \frac{N\,\overline{\Sigma XY} - \overline{\Sigma Y}\,\overline{\Sigma X}}{\sqrt{[N\,\overline{\Sigma X^2} - (\Sigma X)^2][N\,\overline{\Sigma Y^2} - (\Sigma Y)^2]}}$$

N = number of plots, 126 in this study
X = rate of infiltration
Y = other variant; i.e., organic matter

Type of vegetation

The mean rates of infiltration for wet runs on the 24 grassland, 39 woodland, and 63 desert-shrub plots were 1.55, 1.24, and 0.71 inches an hour. The difference in the average final rate of infiltration of the grassland and woodland plots, 0.31 inch, is not significant. The difference of 0.84 inch between the grassland and shrub is highly significant, as is that of 0.52 inch between the woodland and the shrub.

Organic matter

In the profiles studied, the average organic matter content was about 2.5 per cent. Though the infiltration rate tended to increase with increase of organic matter, computation of the simple correlation coefficient showed no statistical significance. As noted earlier, other workers have shown significant correlation between these factors. There are logical reasons why these should be related. For example, it is a generally accepted fact that organic matter affects the aggregation of soil particles, which in turn is closely allied with water movement phenomena. In this study, organic matter of the surface $\frac{1}{4}$-inch was found to be correlated with vegetal density ($r = 0.26$), and this was correlated with the dispersion ratio of the first $\frac{1}{4}$-inch. There was, in turn, correlation between organic matter and dispersion ratio at both the first (0- — $\frac{1}{4}$-inch) depth ($r = -0.53$) and the second ($\frac{1}{4}$- -15-inch) depth ($r = -0.27$). The dispersion ratio was significantly correlated with the infiltration rate.

These interrelationships between soil structure, organic matter, vegetation, dispersion, and water movement are complex phenomena not fully expressed by the computation of simple linear correlation.

The grassland plots had a mean organic matter content of 3.69 per cent; the woodland, 2.98; and the desert-shrub, 1.77. The difference of approximately 0.7 per cent between the grassland the the woodland plots is significant. The difference of approximately 1.9 per cent between the desert-shrub and the grassland plots is highly significant, as is that of 1.2 per cent between the woodland and the desert-shrub plots.

Soil texture

The mean final infiltration rates of the soil profiles studied vary with soil texture, as shown in table 2. There is a statistical significance only in the differences between clay and clay loam, and between clay and sandy loam. The texture influences infiltration probably through the phenomenon of colloid swelling.

Dispersion

The infiltration rate is significantly correlated with the amount of dispersed clay in the soil in both the first and second depths ($r = -0.30$ and -0.35 respectively). It is also correlated with the ratio of dispersed clay to total clay content in both depths. In this study it was found that the dispersion ratio varied inversely as the organic matter.

Factors correlated with infiltration rate

The characteristics of soil and vegetation that are statistically correlated with infiltration rate are summarized in table 3, which shows the computed correlation coefficients.

TABLE 2

Relation of soil texture to infiltration rate

TEXTURE	NUMBER OF PLOTS	INFILTRATION RATE OF WET RUN
		in./hr.
Sandy loam	13	1.42
Sandy clay loam	20	1.22
Clay loam	36	1.07
Clay	57	0.86

TABLE 3

Correlation coefficients of certain soil characteristics determined for two depth zones†

FACTOR	CORRELATION OF VARIOUS FACTORS AT TWO DEPTHS								FIELD MOISTURE CAPACITY‡
	Infiltration		Vegetal density		Dispersion ratio		Moisture equivalent		
	Depth zone		Depth zone		Depth zone		Depth zone		
	0-½ inch	½-15 inches	0-½ inch	½-15 inches	0-½ inch	½-15 inches	0-½ inch	½-15 inches	
Vegetal density	0.46**				−0.10				
Organic matter	0.07	0.08	0.26	0.04	−0.53	−0.27			
Slope	0.14								
Dispersed clay	−0.30**	−0.35**							
Dispersion ratio	−0.31**	−0.31**	−0.10						
Clay (5-μ)	−0.06	−0.19*						0.65	
Clay (2-μ)	−0 04	−0.15							
Silt+clay	−0.15	−0.30**						0 22	
Moisture equivalent	−0.15	−0.12							0.89

* Significant at the 5 per cent point.

** Significant at the 1 per cent point.

† Data for 126 plots. Highly significant if value of $r = 0.23$ at 1 per cent point.

‡ Data for 122 plots instead of 126 plots.

Effect of initial moisture on infiltration rate

Comparison of infiltration rates determined by the runs on dry soil and on the same plots 24 hours later showed that initial moisture is as important as any other factor in governing the rate of infiltration. The average soil moisture at the beginning of the dry run was about 30–40 per cent of the field moisture capacity at the beginning of the wet run.

The infiltration rate decreased to a constant value in approximately 35 to 45 minutes after beginning of rainfall for both the wet and dry runs. This constant value averaged about 0.90 inch an hour higher for the dry than the wet run.

EVALUATION OF FLOOD CONTROL MEASURES IN TERMS OF INFILTRATION

Control of grazing has been shown (3) to have an important effect on vegetation. The ability of vegetation to respond to grazing reduction depends on soil characteristics, precipitation, erosion conditions, and other interrelated factors. In connection with the recent flood control survey of the Department of Agriculture, estimates of potential forage production were made during the field examination. From the estimates of increased vegetal density expected as a result of controlled grazing, estimates of consequent increased infiltration rates were computed from the infiltration data presented in this paper.

As an example of the effect of a change in infiltration rates as a result of increased density, a synthetic hydrograph was constructed to approximate as closely as possible the flood hydrograph from a tributary to Pecos River, the Macho Draw, from which came a significant portion of the damaging flood of June, 1937. It was estimated that the infiltration rate at the time of the flood averaged 0.30 inch an hour. Under proper management, the increased vegetal density probably would increase the infiltration rate to 0.50 inch. This increase would, for the conditions assumed, decrease the flood peak 20 to 30 per cent. Similar computation of flood peak reduction for other tributaries showed comparable decreases.

It is understood that estimates of possible increase of vegetal density for a given area may be in error, but under the assumed conditions, this study has shown that the increase of infiltration rate, with other conditions remaining constant, may decrease the peak of flash floods by as much as 25 per cent. The significance of such a decrease in flood peak is self-evident.

SUMMARY

Artificial rainfall was applied to 264 plots, 12- by 30-inches, representing various soil and vegetal types in the Pecos watershed. In general the soils were shallow, calcareous, heavy in texture, slightly alkaline in reaction (pH 7.6–8.5), and developed under an annual rainfall of 12–18 inches. The predominant vegetal types were desert shrub, grassland, and piñon-juniper woodland.

Soil samples from 126 plots were analyzed in the laboratory, and the data analyzed by statistical methods. The investigation showed a highly significant positive linear correlation between the final infiltration rate and vegetal density. The rate of infiltration showed a highly significant negative correlation with dispersion ratio, amount of dispersed clay, and silt plus clay. The 5-μ clay content showed a significant negative correlation with the final rate of infiltration.

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RESISTANCE OF CLAY-ADSORBED PROTEINS TO PROTEOLYTIC HYDROLYSIS[1]

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When proteinaceous plant or animal tissues are applied to a soil, under favorable climatic conditions, they undergo biological-enzymatic-hydrolytic reactions to form more readily water-soluble and more basic organic and inorganic compounds of nitrogen. Since proteins have been found to be adsorbed by certain clay minerals, the present investigation was undertaken to determine whether a combination of proteinaceous materials and clay minerals would affect the rate of enzymatic hydrolysis of the protein group.

The work of several investigators suggests that clay-adsorbed organic materials may be resistant to biological decomposition. Waksman (5) makes the following statement: "... clay colloid forms compounds with humus colloid, thus preventing its rapid decomposition; it is, therefore, easier to build up the humus content in a clay rich soil than in a clay poor soil." Mattson (4) expressed the belief that adsorbed proteins might be more resistant than free proteins to microbial decomposition. He referred to the use of aluminum salts as tanning agents as an indication of the resistance of aluminum proteinates to decomposition. Thomas Graham (2) found that a complex containing 100 parts of silicic acid and 92 parts of gelatin did not putrefy in a moist state.

Ensminger and Gieseking (1) observed that protein-montmorillonite complexes prepared for base-exchange measurements, in which relatively large amounts of protein were found to be strongly adsorbed as cations, showed only a slight tendency to putrefy. As a result of these observations the present investigation was planned.

EXPERIMENTAL TECHNIC

The following colloids were used: <0.5-μ Wyoming bentonite (predominantly montmorillonite), <1-μ colloid derived from Maquoketa shale and kaolinite. The Maquoketa colloid was isolated from a sample of plastic Wisconsin till from which the Clarence soils, as identified by the Illinois soil survey, were developed. The kaolinite used was a South Carolina variety. The clays for this study were selected because of their rather wide variation in base-exchange capacities and clay mineral types.

[1] Contribution from the department of agronomy, University of Illinois Agricultural Experiment Station. Published with the approval of the director of the experiment station.

[2] Assistant agricultural chemist, University of Idaho, and assistant professor of soil physics, University of Illinois, respectively. The writers are indebted to R. S. Smith for his continued interest and cooperation in this study.

Pepsin and pancreatin[3] were the proteolytic enzymes selected for these experiments. Since pepsin is active only in acid media, and pancreatin is active only in alkaline media, the rate of hydrolysis of proteins could be measured in both acid and alkaline suspensions.

The complexes for pepsin hydrolysis were prepared by mixing the protein with electrodialyzed clay and acidifying to pH 2.25 with either HCl or H_2SO_4. For pancreatin hydrolysis, alkaline suspensions of protein and clay were mixed together and the pH was adjusted to 8.5 with NaOH. Half of the pepsin and pancreatin was added to the protein-clay mixture at the start and the remainder when one half of the digestion time had elapsed. The digestion time ranged from 3 to 6 days at a temperature of 38 ± 2°C. At the end of the digestion, trichloroacetic acid was added to precipitate the unhydrolyzed protein. The complex was then filtered, and total nitrogen was determined in the filtrate.

Proteolytic enzymes, rather than microorganisms, were used in this study for two reasons: first, microorganisms hydrolyze proteins by producing enzymes; second, the hydrolyzing power of enzymes is affected mainly by temperature and pH, which can be controlled within narrow limits, whereas the activity of microorganisms is affected by a great variety of additional factors.

The experiments were designed in such a way that comparisons could be made between protein-clay complexes with no enzyme added, complexes with the same ratio of protein to clay and with the enzyme added after the preparation of the complex, complexes prepared by mixing previously enzyme-hydrolyzed protein to the clay, and finally the protein plus the enzyme in the absence of the clay. The first of these determinations was made in order to show the effectiveness of the clay and trichloroacetic acid in removing the unhydrolyzed protein from the filtrate. The last of the determinations shows the ultimate amount of soluble nitrogen that could be expected if the clay should have no effect whatever upon the hydrolysis of protein in the clay complexes. A comparison of the second and third determinations mentioned above, shows the effect of the clay on the hydrolysis of previously adsorbed proteins.

DISCUSSION OF RESULTS

When a protein molecule is split through a peptid linkage by hydrolysis, one equivalent of nonbasic nitrogen is converted to an equivalent of basic nitrogen. If we assume a set of ideal conditions in which all the nitrogen in a protein was in the form of alpha amino acids, all of which were originally combined through peptid linkages, and subsequently the protein was completely hydrolyzed, then all the nitrogen contained in the original protein will have become basic. This means that proteins (which are generally assumed to contain 16 per cent nitrogen) would provide, under such ideal conditions, approximately 11 m.e. of basic nitrogen per gram. If these same conditions are assumed for the experiments reported in tables 1–4, it is seen that the number of milliequivalents of nitrogen added is more than 10 times the capacity of the clay with the highest

[3] The pepsin was obtained from Merck and Company; and the pancreatin, from The Cudahy Packing Company.

base-exchange capacity. Since the clay could adsorb only one tenth of the nitrogen added and since trichloroacetic acid does not precipitate the simpler polypeptids or amino acids, any simple polypeptid or amino acid nitrogen in

TABLE 1

Influence of Wyoming bentonite on hydrolysis of albumen and hemoglobin by pepsin

SAMPLE NUMBER	COMPOSITION OF PROTEIN-CLAY COMPLEX	AMOUNT OF PEPSIN ADDED	SOLUBLE NITROGEN IN FILTRATE*
		gm.	*mgm.*
1	1 gm. bentonite + 1 gm. albumen	0	3.0
2	1 gm. bentonite + 1 gm. albumen	0.1	42.0
3	1 gm. bentonite + 1 gm. pepsin-hydrolyzed albumen	0.1	82.0
4	1 gm. albumen	0.1	147.0
3 minus 2			40.0
5	1 gm. bentonite + 1 gm. hemoglobin	0	2.2
6	1 gm. bentonite + 1 gm. hemoglobin	0.1	93.0
7	1 gm. bentonite + 1 gm. pepsin-hydrolyzed hemoglobin	0.1	112.0
8	1 gm. hemoglobin	0.1	172.5
7 minus 6			19.0

* Digested 3 days at 38°C.

TABLE 2

Influence of Wyoming bentonite on hydrolysis of albumen and hemoglobin by pancreatin

SAMPLE NUMBER	COMPOSITION OF PROTEIN-CLAY COMPLEX	AMOUNT OF PANCREATIN ADDED	SOLUBLE NITROGEN IN FILTRATE*
		gm.	*mgm.*
9	1 gm. bentonite + 1 gm. albumen	0	4.0
10	1 gm. bentonite + 1 gm. albumen	0.1	8.5
11	1 gm. bentonite + 1 gm. pancreatin-hydrolyzed albumen	0.1	37.0
12	1 gm. albumen	0.1	72.5
11 minus 10			28.5
13	1 gm. bentonite + 1 gm. hemoglobin	0	4.0
14	1 gm. bentonite + 1 gm. hemoglobin	0.1	10.5
15	1 gm. bentonite + 1 gm. pancreatin-hydrolyzed hemoglobin	0.1	69.5
16	1 gm. hemoglobin	0.1	99.0
15 minus 14			59.0

* Digested 6 days at 38°C.

excess of 10 per cent of the amount added should remain in solution in the filtrate and subsequently be measured by the procedure used. Though these ideal conditions were not fully attained in this investigation, they are discussed at this point in order to picture more clearly the principles involved.

It is evident from the data in table 4 that kaolinite, a clay mineral with a very

low base-exchange capacity, has no significant effect on the hydrolysis of albumen and hemoglobin. On the other hand, the base-exchange clays (Clarence clay and Wyoming bentonite) when mutually adsorbed with proteins, interfere

TABLE 3

Influence of Maquoketa shale (Clarence clay) on the hydrolysis of albumen by pancreatin and pepsin

SAMPLE NUMBER	COMPOSITION OF COMPLEX	AMOUNT OF ENZYME ADDED	SOLUBLE NITROGEN IN FILTRATE*
			mgm.
17	4 gm. Clarence clay + 1 gm. albumen	none	20.0
18	4 gm. Clarence clay + 1 gm. albumen	0.1 gm. pancreatin	46.0
19	4 gm. Clarence clay + 1 gm. pancreatin-hydrolyzed albumen	0.1 gm. pancreatin	78.0
19 minus 18	Effect of Clarence clay		32.0
20	4 gm. Clarence clay + 1 gm. albumen	0.1 gm. pepsin	83.0
21	4 gm. Clarence clay + 1 gm. pepsin-hydrolyzed albumen	0.1 gm. pepsin	102.0
21 minus 20	Effect of Clarence clay		19.0

* Digested 5 days at 38°C.

TABLE 4

Influence of kaolinite on hydrolysis of hemoglobin and albumen by pancreatin and pepsin

SAMPLE NUMBER	COMPOSITION OF CLAY-PROTEIN COMPLEX	AMOUNT OF ENZYME ADDED	SOLUBLE NITROGEN IN FILTRATE*
			mgm.
22	1 gm. kaolinite + 1 gm. hemoglobin	none	7.0
23	1 gm. kaolinite + 1 gm. hemoglobin	0.1 gm. pancreatin	79.5
24	1 gm. kaolinite + 1 gm. pancreatin-hydrolyzed hemoglobin	0.1 gm. pancreatin	81.0
25	1 gm. hemoglobin	0.1 gm. pancreatin	87.5
26	1 gm. kaolinite + 1 gm. albumen	none	20.0
27	1 gm. kaolinite + 1 gm. albumen	0.1 gm. pancreatin	64.0
28	1 gm. kaolinite + 1 gm. pancreatin-hydrolyzed albumen	0.1 gm. pancreatin	66.0
29	1 gm. albumen	0.1 gm. pancreatin	73.5
30	1 gm. kaolinite + 1 gm. albumen	none	12.0
31	1 gm. kaolinite + 1 gm. albumen	0.1 gm. pepsin	140.0
32	1 gm. kaolinite + 1 gm. pepsin-hydrolyzed albumen	0.1 gm. pepsin	140.0
	1 gm. albumen	0.1 gm. pepsin	145.0

* Digested 5 days at 38°C.

with the enzymatic hydrolysis of the protein in both acid pepsin suspensions and alkaline pancreatin suspensions. This is substantiated by the data in tables 1–3, which show that less nitrogen is found in the filtrates from enzyme-digested proteins when the proteins are added to the clay before the enzyme is added to

the system. Wyoming bentonite with the highest base-exchange capacity shows the greatest influence in retarding the digestion of the adsorbed proteins. The data indicate that the base-exchange capacity of the clay was an inhibiting factor in the enzymatic hydrolysis of the adsorbed proteins.

Two possible explanations may be given for the interference of the base-exchange clays with the hydrolysis of adsorbed proteins: first, there is the possibility that the enzyme was partly adsorbed by the clay and thereby rendered partly inactive; second, the protein molecule when adsorbed by the clay may be oriented in such a way that the active groups are inaccessible to the enzyme. Langmuir and Schaefer (3) tested the activity of pepsin adsorbed on barium stearate films, which were previously treated in various ways, and in every case failure to inactivate the pepsin ensued when the clotting of milk was used as the criterion for activity. In view of the experiments of these two investigators, the second explanation appears more plausible than the first. It is recognized, however, that both the adsorption of substrate and the adsorption of the enzyme may have exerted an influence on the hydrolytic reactions involved in these experiments.

These adsorption reactions might be expected to have a significant effect on the nitrogen and carbon cycles of soils containing appreciable amounts of clay. Proteinaceous materials, when applied to soils, tend to decompose more rapidly than highly carbonaceous materials. In view of the data presented, this tendency would be expected to be minimized, especially when the highly nitrogenous materials are thoroughly incorporated with soils of high clay content and high base-exchange capacities.

CONCLUSIONS

The adsorption of albumen and hemoglobin by base-exchange clays (Wyoming bentonite and Clarence clay) was found to interfere with the enzymatic hydrolysis of these proteins in both acid pepsin suspensions and alkaline pancreatin suspensions.

Kaolinite, a clay mineral with a very low base-exchange capacity, had no significant effect on the hydrolysis of albumen and hemoglobin.

The degree of interference of a clay with the enzymatic hydrolysis of a protein appears to be influenced by the exchange capacity of the clay.

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DETERMINATION OF IRON IN SOILS AND SILICATES BY THE MERCUROUS NITRATE METHOD[1]

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Iron has usually been determined volumetrically by either of two methods, the stannous chloride and the zinc reduction methods,[2] both of which are long. In the total analysis of a soil (or any silicate), the iron is determined after the sesquioxides (Fe_2O_3, Al_2O_3, and TiO_2) have been precipitated, ignited, weighed, and then fused. In using the stannous chloride procedure, one must fuse the sesquioxides with sodium carbonate. This fusion is difficult, especially when the amount of sesquioxides is high. After the fusion and subsequent dissolving of the fused mass, the solution is concentrated, ferric ion reduced to the ferrous state with stannous chloride, and preventive solution added. The titration is then performed with standard potassium permanganate. If one chooses the zinc reduction method, one may fuse the sesquioxides with potassium pyrosulfate. The ferric ion is reduced to the ferrous state by boiling with zinc or by employing a Jones reductor.

Several workers[2] have suggested titrating iron in the ferric state with titanous sulfate, using the thiocyanate ion as an indicator. Titanous sulfate is difficult to use, however, because it oxidizes very readily in air and the titration requires special apparatus.

Recently, Bradbury and Edwards[3] suggested the titration of iron directly in the ferric state, using mercurous nitrate instead of titanous sulfate. Since Bradbury and Edwards worked only in pure solutions without varying the concentration of iron, it was deemed advisable to investigate the effect of varying the quantity of iron and to test the method with special reference to soils and silicates in general.

STANDARDIZATION OF MERCUROUS NITRATE

A solution of $HgNO_3$ approximately 0.05 N was prepared in 5 per cent HNO_3. Five milliliters of 1.0 N HCl is added to a 20-ml. sample of the $HgNO_3$. The HgCl is diluted to a volume of about 200 ml. After 12 hours the precipitate of HgCl is filtered on a weighed Gooch, dried at 105°C., and weighed.

The solution may be restandardized from time to time by titrating it against a standard solution of $FeNH_4(SO_4)_2$. Since the change in normality was insignificant after a year, the initial standardization sufficed.

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

[2] Scott, W. W. 1939 Standard Methods of Chemical Analysis, ed. 5, vol. 1, D. Van Nostrand Co., Inc., N. Y.

[3] Bradbury, F. R., and Edwards, E. G. 1940 A new method for the volumetric determination of ferric iron. *Jour. Soc. Chem. Indus.* 59 (5): 96–98.

PROCEDURE RECOMMENDED IN TITRATING IRON

The iron should be in the ferric state and should not be more than 0.1 *N* with respect to chlorides. The solution (at room temperature) is diluted to a volume of 200–250 ml., and 5 ml. of a 40 per cent solution of NH_4SCN is added. The solution is then titrated with the $HgNO_3$. It should be noted that the solution should be stirred vigorously and the $HgNO_3$ added dropwise and slowly near the endpoint, which is the absence of the red color. The solution becomes turbid when the endpoint is overrun.

If the amount of iron is very small (0.2–2.0 mgm. Fe^{+++}), the titration may be performed in a volume of 25 ml. and a 0.005 *N* solution of $HgNO_3$ employed.

RESULTS

The accuracy of the method in recovering iron from pure solutions may be seen in table 1.

TABLE 1

Recovery of iron from pure solutions by the mercurous nitrate method

Fe^{+++} TAKEN	Fe^{+++} RECOVERED	VOLUME OF SOLUTION	NORMALITY OF $HgNO_3$
mgm.	*mgm.*	*ml.*	
70.5	70.5	200	0.0492
56.4	56.4	200	0 0492
28.2	28.3	200	0.0492
2.40	2.44	25	0.00497
1.20	1.22	25	0.00497
0.60	0.64	25	0.00497
0.24	0.25	25	0.00497

In the determination of iron in a soil or other silicate, several other ions are present in the solution that is to be titrated. The ions usually present are Fe^{+++}, Al^{+++}, Ti^{++++}, Mn^{++}, H^+, K^+, SO_4^{--}, and PO_4^{---}. The effect of various concentrations of these ions was determined, and the data obtained are presented in table 2.

The data in table 2 clearly indicate that none of these ions cause any appreciable error, the largest error occurring when an exceedingly high concentration of phosphate ion was present. This effect of the phosphate ion may be attributed to the decrease in the intensity of the red color due to the formation of un-ionized iron phosphate. As the amount of phosphate present in silicates is very small, however, this error may be neglected.

The possibility that the fusion and subsequent resolution of the sesquioxides might cause the formation of some ferrous ion and hence yield a negative error was also studied. It was found that the solutions of several fused sesquioxide samples failed to show the presence of ferrous ion by the usual tests.

To test further the applicability of the method, several soils and soil colloids were analyzed for iron by both the $HgNO_3$ and $SnCl_2$ methods. The data are presented in table 3.

TABLE 2

Effect of various ions on recovery of iron (Fe^{+++}) from solution by mercurous nitrate method

Volume 200 ml.; $HgNO_3$ = 0.0497 N; 88.8 mgm. Fe^{+++} taken

ION	CONCENTRATION	Fe^{+++} RECOVERED
	mmol	*mgm.*
		88.8
SO_4^{--}	36.0	88.7
	180.0	88.7
	360.0	88.8
Ti^{++++}	0.01	88.8
	0.05	88.8
	0.16	89.0
Mn^{++}	0.04	89.0
	0.22	89.0
	0.65	89.0
Al^{+++}	0.16	89.0
	0.64	88.8
	1.60	88.8
PO_4^{---}	1.60	88.9
	16.0	88.5
	80.0	88.3
H^+	36.0	88.7
	180.0	88.7
	360.0	88.8
K^+	180.0	88.8
All ions	900.0	88.7

TABLE 3

Ferric oxide content of soils and soil colloids as determined by $HgNO_3$ and $SnCl_2$ methods

	Fe_2O_3 CONTENT	
	$HgNO_3$ method	$SnCl_2$ method
	per cent	*per cent*
Colts Neck loam	11.8	11.7
	11.8	11.7
	11.7	
Colts Neck colloid	39.8	39.8
	39.8	
Montalto clay fraction	19.9	19.9
	19.9	19.8
Impure iron oxide	30.9	31.1

Bradbury and Edwards have noted that the $HgNO_3$ method can also be used to determine both ferrous and ferric ion in one solution. The ferrous ion is titrated with $KMnO_4$ to a faint pink endpoint. Since all the iron now exists in the ferric state, the thiocyanate is added and the solution titrated with $HgNO_3$. By simply subtracting the milliequivalents of $KMnO_4$ from the milliequivalents of $HgNO_3$, the amount of ferric ion may be calculated. The amount of ferrous ion is equal to the amount of $KMnO_4$ used.

COMPARATIVE EFFICIENCY OF ORGANIC PHOSPHORUS AND OF SUPERPHOSPHATE IN THE NUTRITION OF PLANTS[1]

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The fixation of phosphorus applied to soils in fertilizers has given rise to speculation as to how to counteract this undesirable phenomenon. Spencer and Stewart (17) found that phosphorus in the organic, un-ionized form of crude calcium ethyl phosphate was effective in increasing positional availability in the soil. Spencer (18) found the chemical availability of the same phosphate to be on a par with that of treble superphosphate in two alkaline and three acid soils. Others have shown that some acid soils retain certain organic and inorganic forms of phosphorus about equally effectively (4, 9).

In this work the relative efficiency of various organic forms of phosphorus was compared with treble superphosphate as a source of phosphorus for plant nutrition in acid soils. The organic compounds used were lecithin, nucleic acid, calcium ethyl phosphate, and phytin.

EXPERIMENTAL METHODS

The plan of study was similar to that suggested by Stephenson and Schuster (20). Where the phosphorus fertilizers were used, all other deficiencies of the soil, except phosphorus, were cared for by supplying a P-minus nutrient solution. For comparison, some pots of soil received P-minus solution, some distilled water, and others a complete nutrient solution, except in the first experiment where the complete nutrient was omitted.

The phosphorus fertilizers were applied in increasing increments, each to a series of four pots at rates equivalent to 1,000, 2,000, 4,000, and 8,000 pounds of 16 per cent superphosphate per 2,000,000 pounds of soil. This supplies 14, 28, 56, and 112 mgm. phosphorus per pot. All except lecithin were applied in dry form and were well mixed with the soil prior to planting the seeds. Lecithin was dissolved in absolute methanol and applied in a concentrated solution to the dry soil and then mixed. Each pot contained 400 gm. of air-dry soil and grew five plants. Only enough nutrient or water was applied by measure to moisten the soils and keep the plants growing. There was no leaching.

STUDIES WITH AIKEN AND SIFTON SOILS

Sunflowers as indicator plants

The soils used in this study are described in the soil survey reports for Marion and Linn Counties (10, p. 4, 6; 21, pp. 12–25). Table 1 summarizes the treat-

[1] Contribution from the soils department, Oregon State College. Published with the approval of the director of the Oregon Agricultural Experiment Station, Corvallis, Oregon, as Technical Paper No. 391.

[2] Former graduate assistant and professor of soils respectively. The authors are indebted to V. E. Spencer, of the Nevada Agricultural Experiment Station, for supplying them with the calcium ethyl phosphate used in these studies.

ments, the yields, and the heights of the 6-week-old plants at the time of harvesting and gives the "index or growth" for the sunflower plants grown on Aiken clay loam and on Sifton gravelly silt loam. The "index of growth" as used by Spulnik, et al. (19) represents the mean of the average height of the plants and

TABLE 1

Effect of phosphorus fertilizer treatments on growth and yield of sunflowers grown on Aiken and Sifton gravelly silt loam in pots

FERTILIZER TREATMENT*	RATE EQUIVALENT TO SUPER.† PER ACRE	AIKEN CLAY LOAM			SIFTON GRAVELLY SILT LOAM		
		Average yield‡ per pot	Average height	Index of growth§	Average yield per pot	Average height	Index of growth
	lb.	*gm.*	*cm.*		*gm.*	*cm.*	
Water only	0	3.5	68.9	82.8	3.1	56.7	77.9
Lecithin	1,000	4.5	66.5	90.7	3.3	56.7	79.7
	2,000	3.6	67.3	83.2	2.1	55.8	61.2
	4,000	4.4	69.8	92.2	3.4	61.1	83.9
	8,000	3.8	65.9	84.6	3.6	64.2	89.3
			Mean	87.7		Mean	78.5
Nucleic acid	1,000	3.4	63.6	78.5	2.5	56.3	71.2
	2,000	3.4	70.0	83.2	2.2	52.8	64.5
	4,000	4.9	65.5	94.0	3.0	57.7	76.8
	8,000	3.4	60.9	76.8	2.9	56.5	75.8
			Mean	83.1		Mean	72.1
Calcium ethyl phosphate	1,000	3.3	65.4	78.6	2.4	56.1	70.0
	2,000	3.9	69 2	87.4	3.6	63.0	88.3
	4,000	4.7	68.1	94.3	3.4	63.3	85.8
	8,000	4.6	62.0	89.0	4.5	62.9	97.4
			Mean	87.3		Mean	85.4
Treble superphosphate	1,000	4.3	63.7	86.9	2.8	58.1	79.1
	2,000	4.1	66.2	86.7	3.3	61.4	83.0
	4,000	4.7	65.8	92.3	3.8	65.6	92.0
	8,000	5.2	60.0	92.9	4.5	65.6	100.0
			Mean	89.7		Mean	88.5
P-minus	0	3.8	59.5	79.0	2.9	57.0	80.0

* All except "water only" received P-minus solution as needed.

† "Super." is used in this paper as an abbreviation for 16 per cent superphosphate

‡ "Average yield" represents dry weight of sunflower tops.

§ "Index of growth," as used by Spulnik et al. (19).

their total weight expressed in per cent based upon 100 per cent as the maximum of each of these values found in the experiment with a single soil.

Although the data represent the results obtained from 20 plants in four pots, the variations were small and rather inconsistent. On the Aiken soil, no superiority in plant growth from any treatment can be noted, and the plants gave

no indications of marked phosphorus deficiency. Chemical analyses were made upon the plants grown with the maximum treatments of various phosphorus fertilizers and on the checks to determine the relative phosphorus content of the plants. The method of analysis was that outlined by Bertramson (2). The results are summarized in table 2. The Aiken and Sifton soils (table 7) by the Dickman and De Turk method of analysis (5) showed 355 and 2,720 p.p.m. of phosphorus respectively, yet the plants were able to absorb much more phosphorus from the Aiken than from the Sifton soil. Even though, by various chemical tests, the Aiken soil manifests a great fixing power, perhaps in part due to the nature of the clay colloid (3), a fair supply of phosphorus is liberated to the plant.

Treble superphosphate was the most effective in supplying phosphorus to the plants on both soils, followed by the simplest of the organics, calcium ethyl

TABLE 2

Phosphorus absorbed by sunflowers from soil treated with various phosphorus fertilizers

FERTILIZER TREATMENT	PHOSPHORUS ADDED TO THE SOIL	TOTAL PHOSPHORUS ABSORBED*	
		Aiken soil	Sifton soil
	mgm.	*mgm.*	*mgm*
Water only	0	3.9	2.9
Lecithin	112	5.8	3.9
Nucleic acid	112	6.0	2.5
Calcium ethyl phosphate	112	8.6	4.6
Treble superphosphate	112	11.0	5.1
P-minus	0	3.6	2.4

* In this and subsequent tables the milligrams of phosphorus absorbed represents the total in the aerial parts of the plants grown per pot.

phosphate. Lecithin and nucleic acid appeared to be intermediate in efficiency. The P-minus-treated plants absorbed no more phosphorus from the soil than did the plants supplied with distilled water only.

Tomatoes as indicator plants

In view of the lack of response from sunflowers, a similar experiment was initiated with tomatoes, which have been found useful by others (8, 11, 12, 13, 14) as indicator plants in phosphorus nutrition studies. On the Sifton soil, only the maximum fertilizer treatments were used.

Noticeable differences in the tomato plants grown with the various treatments began to appear within 2 weeks after germination. In plants, 2 to 4 weeks old, phosphorus deficiency symptoms were striking. The most noticeable symptoms were the apparent stiffening of the stem; the very dark green color on the dorsal side of the leaves with many purplish specks on the very young leaves, at the base of the epidermal hairs; and the very reddish purple color on the ventral side of the leaves and stems.

TABLE 3

Effect of phosphorus fertilizer treatments on growth, yield, and total phosphorus content of tomatoes grown on Aiken surface soil

FERTILIZER TREATMENT*	PHOSPHORUS ADDED TO THE SOIL	AVERAGE YIELD† PER POT	AVERAGE HEIGHT (AT 9 WEEKS)	INDEX OF GROWTH‡	TOTAL PHOSPHORUS ABSORBED	PHOSPHORUS ABSORBED PER GRAM OF DRY MATTER
	mgm.	gm.	cm.		mgm.	mgm.
Water only	0	0.4	6.1	9.3	0.7	1.8
Lecithin	14	3.5	12.0	25.5	7.3	2.1
	28	3.8	13.1	27.6	6.1	1.6
	56	8.6	21.3	51.1	13.5	1.6
	112	8.1	27.8	58.9	14.7	1.8
			Mean	40.8	10.4	1.8
Nucleic acid	14	5.1	16.0	35.0	8.0	1.6
	28	10.1	24.6	59.4	16.0	1.6
	56	12.0	31.9	74.5	23.2	1.9
	112	16.8	32.9	88.1	38.4	2.3
			Mean	64.3	21.4	1.9
Calcium ethyl phosphate	14	3.7	13.7	28.1	5.7	1.5
	28	7.8	21.7	49.6	10.8	1.4
	56	15.0	36.6	88.4	23.0	1.5
	112	17.5	35.3	93.1	41.0	2.3
			Mean	64.8	20.1	1.7
Treble superphosphate	14	4.6	17.1	35.3	6.7	1.5
	28	11.1	32.0	72.2	25.4	2.3
	56	15.4	36.2	89.1	33.7	2.2
	112	16.9	35.0	91.1	45.0	2.7
			Mean	71.9	27.7	2.2
P-minus	0	1.3	8.1	14.4	2.7	2.0
Complete nutrient	217	19.1	34.2	95.9	67.7	3.5
Phytin	14	2.1	8.7	17.3	5.3	2.5
	28	2.1	8.6	17.1	3.2	1.5
	56	1.6	8.6	15.9	2.9	1.8
	112	5.8	14.6	34.7	8.3	1.4
			Mean	21.3	4.9	1.8
Compost	315	19.5	28.6	89.1	59.6	3.1

* All except "water only" received P-minus solution as needed.
† Dry weight of 3-month-old tomato tops.
‡ As used by Spulnik et al. (19).

The height of the tomato plants was measured 9 weeks after planting, and the dry weights of the aerial parts, harvested at 3 months, were determined. The index of growth and the phosphorus absorbed by the plants are summarized

in tables 3 and 4 for the Aiken and Sifton soils, respectively. Marked phosphorus deficiency symptoms were reflected in the height and weight of the plants and in the phosphorus absorbed. Plants grown with the treatments water only and P-minus were decidedly inferior, especially on the Aiken soil. The marked differences in plants receiving the maximum treatments on the Aiken and the Sifton soil are shown in figures 1 and 2, respectively.

Tomatoes responded to phosphorus on the Sifton soil where the 50 gm. of greenhouse compost was added. Yields compared favorably with the best yields on the Aiken. This compost was found by analysis by the Dickman and De Turk method (table 7) to contain 8,805 p.p.m. of phosphorus, only 7.4 per cent of which was organic. The compost added was equivalent in phosphorus

TABLE 4

Effect of phosphorus fertilizer treatments on growth, yield, and total phosphorus content of tomatoes grown on Sifton surface soil

FERTILIZER TREATMENT*	PHOSPHORUS ADDED TO THE SOIL	AVERAGE YIELD† PER POT	AVERAGE HEIGHT (AT 9 WEEKS)	INDEX OF GROWTH‡	TOTAL PHOSPHORUS ABSORBED	PHOSPHORUS ABSORBED PER GRAM OF DRY MATTER
	mgm.	*gm.*	*cm.*		*mgm.*	*mgm.*
Water only	0	0.4	2.9	4.8	0.1	2.5
Lecithin	112	0.4	5.1	9.1	0.6	1.5
Nucleic acid	112	2.2	8.1	18.0	2.3	1.0
Calcium ethyl phosphate	112	5.3	14.9	36.3	5.5	1.0
Treble superphosphate	112	3.2	10.2	23.8	3.5	1.1
P-minus	0	0.2	5.7	9.7	0.3	1.5
Complete nutrient	217	15.3	27.2	79.5	42.0	2.8
Phytin	112	0.4	4.9	8.6	0.8	2.0
Compost	315	21.2	31.3	100.0	44.0	2.1

* All except "water only" received P-minus solution as needed.

† Dry weight of 3-month-old tomato tops.

‡ As used by Spulnik et al. (19).

to a 22,500-pound application of superphosphate per 2,000,000 pounds of soil. Only this heavy treatment and the complete nutrient furnished phosphorus in a form suitable for maximum plant growth. The relative efficiency of the various phosphorus fertilizers on the Sifton soil was calcium ethyl phosphate first, followed by treble superphosphate, nucleic acid, lecithin, and phytin.

When the phosphorus was applied on the Aiken soil in the form of nucleic acid, calcium ethyl phosphate, or treble superphosphate, the amount absorbed increased nearly in proportion to the increasing increments of fertilizer applied. Where phytin was applied, increasing increments did not result in greater absorption of phosphorus until the maximum treatment was reached. The amount absorbed then was only the equivalent of that absorbed with the smallest addition of the other phosphorus fertilizers.

The relative efficiency of the fertilizers in supplying phosphorus to the plants grown on the Aiken soil, as indicated by the mean value for the four increasing

increment treatments was treble superphosphate first, followed in decreasing order by nucleic acid, calcium ethyl phosphate, lecithin, and phytin. The difference between phosphorus absorbed from nucleic acid and calcium ethyl

TABLE 5

Yield of second crop of tomatoes from original phosphate treatments

ORIGINAL FERTILIZER TREATMENT	RATE EQUIVALENT TO SUPER. PER ACRE	AVERAGE YIELD PER POT	
		Aiken soil	Sifton soil
	lb.	*gm.*	*gm.*
Water only	0	2.4	0.2
Lecithin	1,000	5.2	....
	2,000	4.1	....
	4,000	4.5	....
	8,000	5.6	0.3
Nucleic acid	1,000	4.8	....
	2,000	5.0	...
	4,000	5.6	....
	8,000	6.1	0.2
Calcium ethyl phosphate	1,000	2.6	...
	2,000	5.2	..
	4,000	5.8	..
	8,000	6.4	0.3
Treble superphosphate	1,000	4.6	
	2,000	5.4	.
	4,000	5 9	.
	8,000	7.2	0.2
P-minus	0	5.3	0.1
Complete nutrient	......	13.5	14.8
Phytin	1,000	5.5	...
	2,000	3.2	. .
	4,000	3.6	.
	8,000	4.6	0.3
Compost	22,500	10.6	9.5

phosphate was negligible. The plant responses to increasing increments of the various fertilizers on the Aiken soil are shown in figures 3 to 7.

The inorganic treble superphosphate gave best responses on the Aiken soil. On the Sifton soil the results were somewhat questionable because of the peculiar growth and inconsistent results obtained, but the treble superphosphate was nearly as effective as calcium ethyl phosphate. Perhaps, however, the organic forms may serve as a constant source of phosphorus which over a period of time

would excel the inorganic fertilizer. To check this, the soils used in the foregoing experiments were dried, sieved, and again placed in the respective pots and planted to tomatoes. The controls and the pots receiving complete nutrients were treated as in the initial experiment, but no additions of phosphorus fertilizers were made to the pots in which the different forms of phosphorus had been compared.

The data of table 5 indicate no greater holdover effects from the organic phosphates than from the superphosphate. Yield differences with different rates of treatment are considerably less for the second than for the first crop, indicating a considerable fixation of phosphorus by the soil, as the two crops by no means utilized all the phosphorus added in the heavier treatments. Apparently no treatment had sufficient holdover effect to supply adequate phosphorus for maximum plant growth, as indicated by comparisons with the complete nutrient and with the compost treatments.

STUDIES WITH MELBOURNE SOIL

Table 6 summarizes the yields and phosphorus analysis of tomato plants grown on acid Melbourne clay loam surface (0–6 inches) and subsurface (12–24 inches) soil. The total and inorganic phosphorus of the plant material was determined according to the method outlined by Bertramson (2). The organic fraction represents the difference between the total and the inorganic phosphorus. This is expressed as a percentage, based upon the total phosphorus in each case as 100 per cent.

The maximum response on the surface soil was obtained with treble superphosphate. Following in decreasing order of efficiency were lecithin, calcium ethyl phosphate, nucleic acid, and phytin. The mean for the indexes of growth from the phytin treatments was comparable to the value for the checks where no phosphorus was applied. The mean for phosphorus absorbed into the aerial portion of the plants was the greatest for treble superphosphate followed by calcium ethyl phosphate, nucleic acid, lecithin, and phytin. The relative efficiency of the various forms of phosphorus agreed with that found on the Aiken and Sifton soils.

A marked difference in response to lecithin treatments on the subsurface soil compared with the surface soil is observed. The maximum response in growth and phosphorus absorption on the subsurface soil was found where treble superphosphate was applied. The effectiveness of the organics was in the following decreasing order: calcium ethyl phosphate, nucleic acid, lecithin, and phytin. The response to phytin treatments was for the most part negative.

ORGANIC PHOSPHORUS OF OREGON SOILS

It has been observed that although the organic phosphorus content may be high, the phosphorus availability of the soil for plants may be low (1, 15, 22). Total and inorganic phosphorus analyses were made on the soils used in the previous study together with several of each group of hill and old valley-filling and a few immature valley soils of western Oregon. The results of the analyses,

TABLE 6

Effect of phosphorus fertilizer treatments on growth, yield, and phosphorus analysis of tomato plants grown on Melbourne clay loam

FERTILIZER TREATMENT*	PHOSPHORUS ADDED TO THE SOIL	SURFACE SOIL (0-6 INCHES)			SUBSURFACE SOIL (12-24 INCHES)		
		Index of growth†	Total phos-phorus absorbed	Organic phos-phorus fraction	Index of growth†	Total phos-phorus absorbed	Organic phos-phorus fraction
	mgm.		*mgm.*	*per cent*		*mgm.*	*per cent*
Water only	0	21.3	1.0	41.4	9.0	0.2	....
Lecithin	14	44.4	2.1	46.7	17.2	1.4	....
	28	57.8	3.6	38.8	....	...	..
	56	62.3	4.5	43.7	37.4	3.1	57.3
	112	45.1	5.6	45.8	36.5	3.8	56.7
	Mean	52.4	4.0	43.8	30.4‡	2.8‡	57.0‡
Nucleic acid	14	31.0	1.2	40.8	19.4	0.8	53.7
	28	40.9	1.9	46.0	25.3	0.7	55.2
	56	49.9	3.6	43.9	55.6	3.1	53.4
	112	63.9	11.5	41.7	78.4	7.2	46.3
	Mean	46.4	4.6	43.1	44.7	3.0	52.2
Calcium ethyl phosphate	14	31.9	1.1	52.3	24.8	1.1	51.6
	28	48.3	3.2	60.3	34.8	1.7	49.8
	56	60.1	5.0	51.3	50.3	3.4	59.8
	112	59.6	11.5	42.8	89.9	9.9	54.5
	Mean	50.0	5.2	51.7	50.0	4.0	53.9
Treble superphosphate	14	35.8	2.0	52.2	27.0	0.7	56 6
	28	48.2	2.8	41.1	49.8	2.6	51.6
	56	68.7	11.3	48.0	62.6	4.1	45.8
	112	69.6	13.4	43.1	88.9	12.8	51.6
	Mean	55.6	7.4	46.1	57.1	5.1	51.4
P-minus	0	23.1	0.9	56.2	18.3	0.4	52.8
Complete nutrient	217	100.0	68.8	22.8	100.0	48.0	24.0
Phytin	14	29.2	1.3	58.4	14.2	0.4	49.8
	28	21.9	0.5	53.6	15.3	0.4	56.7
	56	22.0	0.8	62.8	15.3	0.4	51.8
	112	24.9	1.3	46.2	21.4	0.7	54.7
	Mean	24.5	1.0	55.3	16.6	0.5	53.3

* All except "water only" received P-minus solution as needed.

† As used by Spulnik et al. (19).

‡ These mean values do not represent all the treatments and as a consequence are probably higher than would have been the case if all the values had been taken into consideration.

which were made by the Dickman and De Turk method (5), are summarized in table 7.

The hill soils contain much less total phosphorus and a much higher percentage

of organic phosphorus than the two groups of valley soils. The mature valley soils contain the greatest amount of total phosphorus and are intermediate in percentage of the organic form. As soils mature, phosphorus apparently tends to accumulate in the residual, difficultly decomposed organic matter in such a form that low availability to plants results. This was the conclusion of Dyer and Wrenshall (7).

The compost of high organic content was found to be extremely high in total phosphorus. The percentage of organic phosphorus, however, was low, indicating that mineralization of the phosphorus had gone largely to completion during the composting.

TABLE 7

Organic phosphorus of some western Oregon soils

SOIL TYPE	PHOSPHORUS CONTENT			
	Inorganic	Organic	Total	Organic fraction
	p.p.m.	*p.p.m.*	*p.p.m.*	*per cent*
Hill soils				
Olympic clay loam	238	430	668	64.4
Aiken clay loam	140	215	355	60.6
Melbourne clay loam				
0–6 inches	96	192	288	66.7
12–24 inches	33	84	117	71.8
			Mean 357	65.9
Old valley-filling soils				
Sifton gravelly silt loam	1,945	775	2,720	28.5
Powell silt loam	1,166	278	1,444	19.3
Willamette silt loam	604	274	878	31.2
Amity clay loam	536	336	872	38.5
			Mean 1,479	29.4
Recent valley soils				
Chehalis silt loam	862	201	1,063	18.9
Newberg sandy loam	652	210	862	24.4
Sauvie silt loam	410	206	616	33.4
			Mean 848	25.6
Compost	8,150	650	8,805	7.4

DISCUSSION

In this study calcium ethyl phosphate was on a par with treble superphosphate as a source of phosphorus for plant growth. On the basis of phosphorus content of the plants, the treble superphosphate in nearly every case resulted in appreciably higher values than those for calcium ethyl phosphate, which in turn excelled those for the other organics.

The relative efficiency of the organics as phosphorus fertilizers is apparently correlated with their simplicity of molecular structure and ease of decomposition.

Tests conducted in this laboratory to discover the ease with which the various organic compounds in solution were decomposed and converted to inorganic phosphorus by microorganisms showed that calcium ethyl phosphate was the most easily hydrolyzed, nucleic acid was next, followed by lecithin. Their relative efficiency as fertilizer decreased in the same order. The phytin probably was precipitated by iron or rendered ineffective by some other insoluble combination in the soil, as suggested by Dyer and Wrenshall (6).

There was no indication that the organic fertilizers effected an increase in the percentage of organic phosphorus in the plant. No increase was expected, as Weissflog and Mengdehl (23), even where they obtained great increases in growth with the organic phosphorus in sterile cultures, found a slight increase in organic phosphorus content only in the roots of the plants grown in nutrient solutions with phytin, nucleic acid, and glycerophosphoric acid as the source of phosphorus. Where simpler organic phosphorus compounds were used, hydrolysis was apparently effected in the culture medium or immediately upon entry of the compound into the plant.

The survey of organic phosphorus content of pedogenic groups of western Oregon soils indicates that in the older soils the phosphorus tends to accumulate in the form of rather stable organic compounds. It is important to differentiate between this residual organic phosphorus of the soil and the simpler, more easily decomposed organic compounds of crop residues and manures which upon entering the soil are attacked by microorganisms and serve as an immediate supply of inorganic phosphorus for the nutrition of plants.

According to the foregoing study of phosphorus responses on acid soils, the phosphorus nutrition of the plants under normal conditions of growth seems to be chiefly in the inorganic realm. The organics are valuable as phosphorus fertilizers to the extent that they furnish inorganic phosphorus. Plant residues rich in the simpler forms of organic phosphorus may, therefore, serve to supply available inorganic phosphorus on soils of low phosphorus-supplying power. This type of organic material may have a value nearly equal to that of the soluble superphosphates, as a source of phosphorus. Availability of organic phosphorus is, therefore, in part a biological phenomenon (16). The old soils have become biologically inactive, and the old resistant residue of humus no longer decomposes readily or liberates appreciable quantities of phosphorus. This condition is especially noticeable in the Sifton soil, high in organic matter and organic phosphorus but unable to supply much nutrient to the growing plant.

CONCLUSIONS

Soil pot tests were conducted to compare the relative efficiency of various organic and inorganic phosphorus fertilizers on several acid soils.

The superiority of the tomato over the sunflower plant as an indicator of phosphorus deficiency was demonstrated.

The efficiency of the various organic phosphorus fertilizers on acid soils in supplying the immediate needs of the crop, compared with treble superphosphate was in the following order: Treble superphosphate = calcium ethyl phosphate >

nucleic acid > lecithin > phytin. The ease of decomposition of the organics was apparently in the same order, with the exception of phytin, which was probably precipitated in the soil.

Experiments to determine which phosphorus fertilizer was the most efficient in supplying the plants with phosphorus over a long period showed the order of decreasing efficiency as follows: Treble superphosphate = calcium ethyl phosphate > nucleic acid > lecithin for the Aiken soil. The order for Sifton soil was calcium ethyl phosphate = lecithin > water only > nucleic acid = treble superphosphate.

A brief survey of the organic and inorganic phosphorus was made on western Oregon soils. The total phosphorus content of the soils according to groups was: mature valley soils > recent stream-bottom soils > old residual hill soils. The percentage organic of the total phosphorus in these soils by groups was: old residual hill soils > mature valley soils > recent stream-bottom soils. In general, the phosphorus fertility or supplying power of these soils is in an inverse order to that of the organic phosphorus percentage of the total phosphorus.

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PLATE 1

PLANT RESPONSES TO PHOSPHORUS FERTILIZER TREATMENTS ON AIKEN CLAY LOAM AND ON SIFTON GRAVELLY SILT LOAM

Numbers 1, 2, 4, 8, and 22.5 refer to the equivalents in thousand pounds of superphosphate per acre.

FIG. 1. TOMATOES 3 MONTHS OLD GROWING ON AIKEN CLAY LOAM WITH THE MAXIMUM TREATMENTS AS COMPARED TO THE CONTROLS

"Org-phos" means calcium ethyl phosphate. (See table 3.)

FIG. 2. SAME AS FIGURE 1 EXCEPT ON SIFTON GRAVELLY SILT LOAM

(See table 4.)

FIG. 3. TOMATOES GROWING ON AIKEN CLAY LOAM WITH INCREASING INCREMENTS OF TREBLE SUPERPHOSPHATE AS COMPARED TO THE CONTROLS

FIG. 4. SAME AS FIGURE 3, EXCEPT WITH CALCIUM ETHYL PHOSPHATE

FIG. 5. SAME AS FIGURE 3, EXCEPT WITH NUCLEIC ACID

FIG. 6. SAME AS FIGURE 3, EXCEPT WITH LECITHIN

FIG. 7. SAME AS FIGURE 3, EXCEPT WITH PHYTIN

FIG. 1

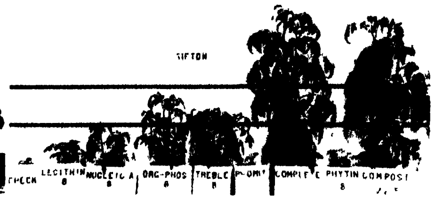

FIG. 2

FIG. 3

FIG. 4

FIG. 5

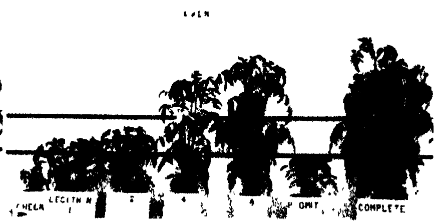

FIG. 6

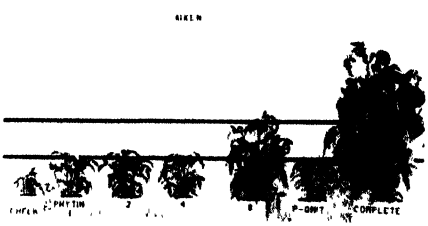

FIG. 7

INOCULATION OF SOIL WITH AZOTOBACTER CHROOCOCCUM[1]

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Many Utah soils when mixed with a suitable carbohydrate and incubated, gain appreciable quantities of nitrogen. A smaller number, if inoculated into a liquid medium, register gains, yet some of them do not contain Azotobacter. This means that some soils which do not naturally contain Azotobacter gain in nitrogen when furnished with a carbohydrate and incubated under appropriate conditions. Hence the questions: Why is Azotobacter absent from these soils, and will the organism survive if inoculated into such soils? Will the inoculated soil show gains in nitrogen if kept under optimum conditions?

Azotobacter does not occur in the soil of the Nephi dry-land substation, situated about 5 miles south of Nephi, Utah, on the north slope of the Levan Ridge. The soil is of the deep dry-farm type derived from the weathering of the adjacent mountain ranges. It is a clay loam, and contains in the surface foot-section, as an average, 4,100 pounds of nitrogen, 7,000 pounds of phosphorus, 86,000 pounds of potassium, 1,480 pounds of sulfur, 42,000 pounds of organic carbon, 69,000 pounds of magnesium carbonate, and 139,000 pounds of calcium carbonate. Consequently, it is rich in most plant-food elements. The limiting factors in crop production of this soil are nitrogen and moisture. The soil has a rich microflora, and when plated on various synthetic media, 12,000,000 to 20,000,000 microorganisms per gram of soil develop. It has an active ammonifying and nitrifying microflora, and when inoculated into nitrogen-free synthetic media or when treated with a suitable carbohydrate fixes appreciable quantities of nitrogen. Repeated search, however, has failed to reveal Azotobacter.

PLAN OF THE EXPERIMENT

The soil used in this experiment was obtained from the surface foot of one of the fallow plots of the Nephi substation. It was transported to Logan, Utah, and then thoroughly mixed, care being taken to prevent contamination with Azotobacter. The soil was analyzed, as outlined later, for nitrogen and nitrogen-fixing powers. It was variously treated as indicated in table 1 and packed into 2-gallon jars, which were placed in the greenhouse in September, 1922. The soil was occasionally watered and was kept bare except during 2 years when crops of wheat were grown. The nitrogen-fixing powers of the soil of the various pots were determined in 1926, 1928, 1932, 1934, and 1941. The nitrogen was determined, in 1922, 1926, 1934, and 1941.

[1] Contribution of the department of bacteriology and biochemistry. Report on research project 22, Adams. Approved for publication by the director.

[2] Research professor and research assistant, respectively.

Nitrogen was determined by the Gunning-Hibbard method; and the nitrogen-fixing powers were determined by the use of a medium of Greaves.[3] The medium was distributed in 100-cc. portions in 500-cc. Erlenmeyer flasks. Each flask was inoculated with 1 gm. of the soil and then incubated at 28° to 30°C., alongside sterile checks, for 21 days, after which the nitrogen was determined. Six replicate determinations were made for each of the various soil treatments; the results reported are the averages.

TABLE 1

Nitrogen fixed in synthetic medium inoculated with variously treated Nephi soils

100 cc. of medium inoculated with 1 gm. of soil, incubated 21 days at 28° to 30° C.

SOIL TREATMENT	NITROGEN FIXED				
	1926	1928	1932	1934	1941
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*
No treatment	0.9	1.9	5.2	6.0	9.3
Autoclaved 6 hours, 15 pounds	0.0	0.0	8.2	8.5	9.0
Inoculated with *Azotobacter chroococcum**	8.9	8.7	11.8	10.0	8.4
5 tons $CaCO_3$ per acre	0.9	1.5	8.7	7.8	8.7
5 tons $CaCO_3$ per acre; inoculated with *Azotobacter chroococcum**	8.7	10.0	11.7	11.5	8.2
10 tons dried horse manure per acre	8.1	8.3	5.2	6.2	9.9
10 tons dried horse manure per acre; 5 tons $CaCO_3$	6.3	6.1	7.5	7.1	6.2
10 tons dried horse manure per acre; 5 tons $CaCO_3$; inoculated with *Azotobacter chroococcum**	17.3	17.3	10.3	11.6	7.9

* The soil was inoculated with Azotobacter in 1922 by mixing a water suspension of the pure culture with the soil.

EXPERIMENTAL RESULTS

The nitrogen-fixing powers of the soil varied from 2.3 to 2.8, with an average of 2.5 mgm. of nitrogen per 100 cc. of medium in 1922. The results of subsequent determinations are given in table 1.

Azotobacter was absent from the soil of all the pots in 1922. In 1926 and 1928, Azotobacter was present in the inoculated soil and in the manure-treated soil. Calcium carbonate had no effect on the establishment of *Azotobacter chroococcum* or on the nitrogen fixed in the soil. The quantity of nitrogen fixed in the synthetic medium inoculated with Azotobacter-treated soil was considerably greater than that in uninoculated soil.

It is evident from these results that Azotobacter not only survives when inoculated into the Nephi soil but rapidly multiplies in it. Hence its absence in this natural soil is due to failure of the organism to reach the soil and not to the absence of required nutrient or to the presence of toxic substances.

From the nitrogen determinations made on the soil in 1922 and at intervals thereafter until the spring of 1941, the gain in nitrogen per acre-foot of soil was

[3] Greaves, J. E. 1933. Some factors influencing nitrogen fixation. *Soil Sci.* 36: 267–280.

calculated. An acre-foot of soil was taken as 3,600,000 pounds. The average results are given in table 2.

Only the soil to which Azotobacter had been added, either as a pure culture or in the manure, contained Azotobacter in 1926. The gains in nitrogen in this year resulting from the addition of organic manure to the soil, however, were significant. In 1934 all samples were found to contain Azotobacter, and those which had received organic manure made the greatest gains. In 1941 there was more nitrogen in the soils that had received organic manure than in the soils which had not received organic manure, and it is possible that the inoculation in addition to the organic manure caused a further increase in nitrogen gains.

The average yearly gain of nitrogen in the soil that received no manure was 27 pounds per acre, whereas that in manure-treated soil was 28 to 38 pounds.

TABLE 2

Nitrogen gained by variously treated Nephi soils kept in pots in the greenhouse from 1922 to 1941

Treatments and results on an acre basis

SOIL TREATMENTS	NITROGEN GAIN				
	1922	1926	1934	1941	Annual
	lbs.	*lbs.*	*lbs*	*lbs.*	*lbs.*
No treatment	0	0	396	504	27
Autoclaved 6 hours, 15 pounds	0	0	396	504	27
Inoculated with *Azotobacter chroococcum*	0	36	324	504	27
5 tons $CaCO_3$	0	0	324	504	27
5 tons $CaCO_3$; inoculated with *Azotobacter chroococcum*	0	36	504	540	28
10 tons dried horse manure	0	152	512	620	33
10 tons dried horse manure; 5 tons $CaCO_3$	0	188	620	620	33
10 tons dried horse manure; 5 tons $CaCO_3$; inoculated with *Azotobacter chroococcum*	0	224	728	728	38

The gain in nitrogen may have come from four different sources: 1. That gained from the atmosphere, ammonia, nitrites, and the like. The greenhouse was isolated from the laboratory and no appreciable quantities of decomposing organic materials which could emit ammonia were near. Consequently, the gain from this source was small. 2. The combined nitrogen carried to the soil by the irrigation water. It was hoped to rule this out by a comparison with the autoclaved soil, but this soil soon became contaminated with nitrogen-fixing organisms. The water used was the city culinary water which contains mere traces of combined nitrogen. Everything therefore points to the conclusion that the gains resulting from the applied irrigation water were small. 3. Nitrogen that may have been in the soil and that was not at first determined by the Kjeldahl method. Nondeterminable pyrrole nitrogen in the soil may have been transformed into nitrogen compounds determinable by the Kjeldahl method.

This has been shown elsewhere[4] to be insignificant for short periods and probably would not have been significant in this work. 4. The quantity fixed by nonsymbiotic bacteria of the soil. It is our opinion that the main gain observed is from this source. This soil at the beginning was low in nitrogen, containing only 0.081 per cent. It is not likely that soils rich in nitrogen would have made even comparable gains, nor is it probable that field soils would have made as large gains as these soils which were kept near an optimum temperature and received much more water than was the case with field soils. It is evident, however, that the addition of organic manure materially increases the nitrogen-fixing powers of this soil, and its addition to field soils probably would materially increase their nitrogen-fixing powers.

SUMMARY

A typical dry-farm soil free from Azotobacter was inoculated with *Azotobacter chroococcum* and variously treated with calcium carbonate and organic manure. The soil was kept bare in a greenhouse for 17 years, and wheat grown 2 years. At intervals the nitrogen-fixing powers and the nitrogen of the soil were determined with the following results:

During the first 12 years of the experiment, inoculated soil when added to a synthetic mannite medium and incubated for 21 days fixed much larger quantities of nitrogen than did uninoculated soil. At the end of 19 years all soils had become contaminated with *Azotobacter chroococcum*; hence, all fixed approximately the same quantities of nitrogen.

The average annual gain of nitrogen per acre-foot varied from 27 to 38 pounds. The uninoculated soil became contaminated with Azotobacter sometime during the first 12 years of the experiment; it cannot be said definitely, therefore, that inoculation of this soil with Azotobacter will increase its nitrogen content. There is some *definite* evidence, however, that the addition of organic manure to the soil increased the quantity of nitrogen gained. It is believed that the gain was due primarily to the activities of nonsymbiotic nitrogen-fixing microorganisms. It is proved that the absence of Azotobacter from this soil is not caused by an unfavorable environment.

[4] Greaves, J. E., and Greaves, J. D. 1932 Nitrogen fixers of leached alkali soil. *Soil Sci.* 34: 375–383.

THE OCCURRENCE OF BACTERIOSTATIC AND BACTERICIDAL SUBSTANCES IN THE SOIL[1]

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It has been demonstrated frequently that the soil contains substances toxic to the growth of higher plants and to microorganisms. Such substances are said to be destroyed by oxidation, by heat, by treatment with various antiseptics, and by means of certain adsorbing agents, such as carbon black. It has been suggested (10) that soil microorganisms are responsible for the production of these toxic substances, though the ability to demonstrate such substances has often depended upon the test organisms employed. Frost (5), for example, could not find in soil any toxin against *Bacillus typhosus*. Greig-Smith recognized this when he said (6) that "doubtless there are as many varieties of toxin as there are groups of bacteria in the soil. It is known that the toxins of one group may not be toxic to another group." By using *B. prodigiosus* as an indicator, he found in the soil thermolabile substances toxic to this organism. The presence of these substances depended largely upon the treatment of the soil. Addition of organic matter, as well as a low moisture content, led to an increase in toxin production; aeration, drying, or chloroforming of soil led to a decrease. The fact that different soils may contain different toxins was also indicated by Hutchinson and Thaysen (8). Lewis (10) found that *Pseudomonas fluorescens* produces toxins in sterilized manured soils; these toxins could be extracted by alcohol and were able to inhibit the growth of such bacteria as *B. cereus*, *B. mycoides*, *B. anthracis*, and *Sarcina lutea*, but not of *Escherichia coli* and *S. marcescens*.

Upon addition of soil extract to culture media, Rybalkina (13) obtained typically deformed cells of *B. mycoides*. The production of the toxic substance was found to be greatly influenced by soil treatment and season of year.

The presence in soils of substances injurious to the growth of higher plants has also been definitely established (14). An attempt has even been made to correlate the occurrence of these substances with the state of exhaustion or infertility of the soil, but this so-called toxin theory of soil fertility has not been substantiated by more extensive investigations and at best finds justification in only very special instances.

Since the soil is known to harbor microorganisms that are antagonistic to the bacteria and fungi responsible for some of the most important soil processes, one may surmise that substances toxic to these organisms will also be produced in the soil. It is not known, however, whether they accumulate in the soil or are rapidly destroyed by other microorganisms. When conditions are made favorable for an increase in microbial activities, as by the addition of stable manures

[1] Journal Series Paper, New Jersey Agricultural Experiment Station, Rutgers University, department of soil microbiology.

and green manures or by improved soil aeration, the rise in activities is soon followed by a drop, until an equilibrium has been established between the different groups of microorganisms inhabiting the soil. This equilibrium may be quite different from that which prevailed in the soil before the stimulating effect was exerted (16). It is characterized, for example, by a reduction in the number of spore-forming bacteria, especially in a vegetative state (3), which may be due to the accumulation of bacteriostatic substances in the soil.

The recent isolation from soil of antagonistic organisms, including spore-forming bacteria (4, 7, 15) and actinomycetes (1, 9, 11, 17), suggested a study of the presence in soil of substances possessing bacteriostatic and bactericidal properties of possible microbial origin. It is known that the action of these substances is selective in nature, being limited, in many instances, to certain groups of bacteria (4), and that the amounts required for inhibiting the growth of other groups of microorganisms vary greatly. The addition of small quantities of some of these substances to agar media, used for plating out soil, prevents the development of many bacteria (18); if sufficient concentrations are added, all soil bacteria, actinomycetes, and fungi can be inhibited from development on the plate (20).

EXPERIMENTAL

A study was made of the presence in the soil itself, of substances that have bacteriostatic and bactericidal properties comparable to those obtained from pure cultures of microorganisms isolated from soil and grown on artificial media (17, 19, 20). Two soils, one low in organic matter and very infertile, 7A, and the other high in organic matter and fertile, 18A, were extracted with ether. These two soils yielded 69 and 62 mgm. of ether-soluble material per 1 kgm. of fresh soil, respectively. Following the ether extraction, the soils were treated with 95 per cent ethyl alcohol, and finally with distilled water. In order to test the action on bacteria of the preparations thus obtained, the ether-soluble material was suspended in alcohol, to give 5 mgm. per 1 cc., and further diluted with water; the alcohol extract was heated on a water bath to remove the alcohol, and the residue was suspended in water; and the water-soluble portion was concentrated to a small volume at 50°C. under reduced pressure.

The three fractions were tested for their bacteriostatic effects by the methods described elsewhere (17). The results, given in table 1, show that the alcohol- and water-soluble fractions had no inhibiting effect on the growth of the test bacteria, but the ether-soluble fraction had a marked inhibition upon *B. subtilis* and *S. lutea* but not upon *E. coli*. It is of interest to note that the extract of the poor soil was more active bacteriostatically than that of the fertile soil. Since 1 kgm. of soil 7A contains 15.5 gm. organic matter, the ether-soluble fraction makes up 0.45 per cent of the total organic matter. On comparing the results of the test with the action of pure actinomycin, which is an ether-soluble substance produced by a soil organism, *Actinomyces antibioticus* (20), 0.1 mgm. of the ether-soluble portion of the soil organic matter is found to be equal in activity to 0.1 microgram of the actinomycin. In other words, 0.1 per cent of the total ether-

soluble material obtained from an exhausted soil is found to be comparable in activity to that of pure actinomycin.

The bactericidal action of the ether-soluble fraction of the soil organic matter was next determined. The results presented in table 2 show that the substance has a marked bactericidal effect on *B. subtilis*.

These results tend to show that the bacteriostatic and bacteriolytic substance present in the soil may be, partly at least, of the actinomycin type. In order to demonstrate whether actinomycin can persist in the soil, the results of the following experiment are reported here. Ten-gram portions of a moist fertile soil, 18B, were placed in test tubes. One set was sterilized and the other left in a fresh state.

TABLE 1

Bacteriostatic action of soil extracts

NATURE OF FRACTION	ETHER-SOLUBLE						ALCOHOL-SOLUBLE						WATER-SOLUBLE					
CONCENTRATION PER 10 CC AGAR *mgm*	0.1		0.3		1.0		0.1		0.3		1.0		0.1		0.3		1.0	
SOIL*	7A	18A	7A	18A	7A	18A	7A	18A	7A	18A	7A	18A	7A	18A	7A	18A	7A	18A
Growth† of test organism																		
E. coli	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
B. subtilis	2	3	0	1	0	0	3	3	3	3	3	3	3	3	3	3	3	3
S. lutea	0	2	0	0	0	0	3	3	3	3	3	3	3	3	3	3	3	3

* 7A = infertile soil; 18A = fertile soil.

† 0 = no growth, or full inhibition; 1 and 2 = limited and fair growth, or partial inhibition; 3 = good growth, or no inhibition.

TABLE 2

Bactericidal action of ether-soluble fraction of soil

B. subtilis grown for 8 hours in nutrient broth used for test

ETHER-SOLUBLE FRACTION ADDED	THOUSANDS OF BACTERIA IN 1 CC. BROTH CULTURE
Start	960
Control culture*	5,330
Alcohol control†	6,040
Ether extract, 1 mgm.	310
Ether extract, 5 mgm.	<10

* Incubation—24 hours at 28°C.

† 0.2 cc. alcohol, equal to amount used with extract, added to 10 cc. broth.

An alcoholic solution of purified actinomycin was evaporated to dryness and suspended in water. Varying amounts of this suspension were added to the two lots of soil and placed in the incubator at 28°C. The unsterile soil was plated out after 3 and 12 days. After 12 days, the actinomycin was extracted from the soil with ether and alcohol. It was redissolved in alcohol and tested for activity upon the basis of the amount originally added to the soils (table 3).

The results obtained tend to indicate that the actinomycin added to fresh soil is largely inactivated, possibly partly through adsorption by the soil particles and partly through its destruction by soil microorganisms. Only a small fraction of the actinomycin remains in the soil in an active state. The addition of small amounts of actinomycin to soil was found to have a favorable effect upon the

TABLE 3

Influence of actinomycin upon the multiplication of microorganisms in fresh soil*

ACTINOMYCIN ADDED PER 10 GM. OF SOIL	AFTER 3 DAYS' INCUBATION		AFTER 12 DAYS' INCUBATION		
	Bacteria	Fungi	Bacteria	Fungi	Residual actinomycin†
micrograms					*micrograms*
0	5,800	65	9,100	270	1
100	8,300	74	13,400	170	3‡
330	15,200	88	16,100	190	7‡
1,000	45,900	85	32,700	180	25‡
3,000	7,600	152	218,000	560	75‡

* Nutrient agar used for plating; numbers given in thousands per 1 gm. of soil.

† As measured by its bacteriostatic action against *B. subtilis*, *B. mycoides*, and *S. lutea*.

‡ The corresponding amounts of actinomycin remaining in sterilized soil were: 20, 66, 200, and 600 micrograms.

TABLE 4

Inhibition of actinomycin by soil and plant constituents*

ACTINOMYCIN ADDED	CONTROL			α-HUMUS FROM PEAT						α-HUMUS FROM STRAW COMPOST					
				1 mgm. per plate			10 mgm. per plate			1 mgm. per plate			10 mgm per plate		
	B. mycoides	*B. subtilis*	*S. lutea*	*B mycoides*	*B. subtilis*	*S. lutea*	*B. mycoides*	*B. subtilis*	*S. lutea*	*B. mycoides*	*B. subtilis*	*S. lutea*	*B. mycoides*	*B. subtilis*	*S. lutea*
micrograms															
0	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
0.5	0	0	0	0	0	0	3	3	3	2	0	0	3	3	3
1.0	0	0	0	0	0	0	3	0	0	0	0	0	3	3	3
3.0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0
10.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

* 0 = no growth, or full inhibition; 2 = fair growth, or partial inhibition; 3 = good growth, or no inhibition.

development of bacteria and especially of fungi. With larger amounts, there is a delay before the stimulating effect becomes marked.

The soil is commonly looked upon as harboring substances that are favorable to the development of microorganisms. The fact that most of these substances are water-soluble compounds gave rise to the use of "soil extract" in many culture media for bacterial growth. It is to be recalled in this connection, that Orla-

Jensen (12) reported the presence in milk, in addition to activators, also of growth-inhibiting substances, both thermostable and thermolabile in nature. One is thus able to demonstrate that soil has a marked resemblance, in this respect, to milk. The survival of specific microorganisms in soil is thus controlled, aside from the nature and supply of energy sources, aeration, and reaction, by the relative concentration of growth-promoting and growth-inhibiting substances. The proponents of the toxic theory of soil fertility also spoke of the simultaneous presence of growth-promoting and growth-inhibiting bodies in the soil solution (2).

In order to determine whether the organic constituents of soils and plants are capable of neutralizing the injurious effect of actinomycin, α-humus fractions (alkali-soluble and acid-precipitated preparations) of lowmoor peat and straw composts were used. Varying amounts of the material were dissolved in very

TABLE 5

Absorption of actinomycin by α-humus extracts*

50 mgm. of material added to 5 cc. water containing actinomycin in solution

ACTINOMYCIN ADDED	CONTROL			α-HUMUS FROM PEAT			α-HUMUS FROM STRAW		
	B mycoides	*B. subtilis*	*S lutea*	*B. mycoides*	*B. subtilis*	*S. lutea*	*B. mycoides*	*B subtilis*	*S. lutea*
micrograms									
0	3	3	3	3	3	3	3	3	3
1	0	0	0	3	1	2	3	3	3
3	0	0	0	1	0	0	3	0	0
10	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0

* 0 = no growth, or full inhibition; 1 and 2 = limited and fair growth, or partial inhibition; 3 = good growth, or no inhibition.

small quantities of dilute alkali solutions and diluted with water. In one experiment, these solutions were sterilized and added to nutrient agar treated with varying concentrations of actinomycin. The plates were streaked with three test bacteria. A definite reduction in the activity of actinomycin was obtained, as shown in table 4.

In another experiment, 50-mgm. portions of the humus preparations were added to 5-cc. portions of water containing different amounts of actinomycin. The containers were placed overnight in a 37°C. incubator. The solutions were then tested for residual actinomycin. The results, given in table 5, show also that the humus extracts of peat and composted straw absorb considerable amounts of actinomycin, or in some other way neutralize its activity.

The organisms used in these tests are most sensitive to actinomycin. Other bacteria, especially the Gram-negative types and the fungi, are less sensitive, as shown elsewhere (18).

These results show conclusively that although antagonistic substances (mi-

crobial toxins) of the actinomycin type may be produced in the soil or may even accumulate there, their action upon the majority of soil organisms is rather limited.[2]

SUMMARY

The results of studies on the presence and activity in soils of bacteriostatic and bactericidal agents of a type found to be produced by organisms isolated from the soil can be summarized as follows:

By the use of proper extracting agents (ether), it is possible to demonstrate that soils contain substances of the actinomycin type, which inhibit the growth of certain bacteria in culture media.

These substances when isolated from the soil have not only a bacteriostatic but also a bactericidal action upon certain bacteria.

When added to the soil, actinomycin, in concentrations much higher than would be necessary to inhibit bacteria in artificial culture media, is rendered ineffective against these bacteria.

Soils, peats, and composts contain a substance (α-humus) that reduces considerably the activity of actinomycin even in artificial culture media.

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SOIL MOISTURE TENSIOMETER MATERIALS AND CONSTRUCTION[1]

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A porous cup when filled with water and connected to a suitable gage may be used for measuring the pressure in soil water (1, 5). This pressure may be either greater or less than atmospheric pressure, which is ordinarily taken as the pressure reference. At points below a water table the pressure is positive, but in unsaturated soil the water in a porous cup must be under negative or vacuum pressure in order to be in equilibrium with the water in the soil. The combination of a porous cup and a vacuum gage for measuring the *equivalent* negative pressure[3] or tension of water in unsaturated soil has been called a "tensiometer" (1).

Improvement in both the design and materials for tensiometer construction will undoubtedly continue, and no one design will be best for all types of use. Care must be exercised in the selection of materials and in the construction of any tensiometer if it is to give trouble-free operation, and sometimes difficulties develop which are not easy to anticipate.

Numerous requests have come to the writer for information on the design and construction of tensiometers. Since these units are not commercially available at present, it is hoped that this paper will be of assistance to those who wish to construct tensiometers for their own use. Three units that have performed satisfactorily under field and laboratory conditions are described.

TENSIOMETER CUPS

Porous cups suitable for use with tensiometers and of almost any desired shape can be made up in the laboratory by the drain-casting process. Experimentation with different clays and firing processes may be necessary to obtain a suitable porous structure. The cup wall should be permeable to water, and yet when the wall is wet the "air-entry value" must be greater than one atmosphere. This value is simply the pressure difference required to produce an air leak through the cup wall when it is saturated with water. There is to a certain extent, a reciprocal relation between these two properties; when one is high the other is low. Experience indicates that the permeability should be as high as possible and still have the air-entry value greater than one atmosphere.

[1] Contribution No. 23 from the U. S. Regional Salinity Laboratory, Bureau of Plant Industry, Riverside, California, in cooperation with the 11 western states.

[2] Senior soil physicist.

[3] The expression "*equivalent* negative pressure" is used because it is not known over what range of soil moisture contents less than saturation, water is actually present in a liquid phase and outside the range of the adhesive force of the soil particles. Actually a tensiometer measures the negative pressure or tension to which the cup water must be subjected to give it the same free energy as the adjacent soil water with which it is in equilibrium.

The air-entry value may be determined by observing the air pressure required to produce air leaks through a tensiometer cup which is submerged in water after it is connected to a controllable compressed air source.

The water conductance of a tensiometer cup is the rate at which a cup transmits water at unit pressure difference. This appears to be a significant constant for a tensiometer and involves the area and thickness of the cup wall as well as the permeability of the porous body. Various methods have been suggested for measuring cup conductance (2).

The porous cups described in this paper are commercially[4] available, and the properties of the porous body appear to be almost ideal. The air-entry value is about two atmospheres, i.e., 30 pounds per square inch. The water conductance for the cups shown in figure 1 averages 0.05 cc. $sec.^{-1}$ $atmos.^{-1}$ for the larger spout top cup K 948, and 0.025 cc. $sec.^{-1}$ $atmos.^{-1}$ for the small gasket seal cup K 980.

TENSIOMETER FOR FIELD USE

A number of factors underlying good tensiometer design have been discussed elsewhere (2) and will not be repeated here. The system should be vacuum-tight, rugged, and arranged so that filling the system completely with boiled hot (air-free) water is a simple operation. Also, convenient means should be provided for detecting and removing any air that subsequently accumulates in the system.

The tensiometer shown in figure 1 A and B is suitable for field installations or where soil space is not limited. The steel tube to which the porous cup is secured by set screws serves as a handle for installing and removing the cup without stressing the vacuum joints. The mercury manometer is supported on the 3-foot length of channel iron which is welded to the steel tube.

A glass air-trap is provided so that air accumulating in the system can be readily detected and removed. Trouble has been experienced with the joint at the ends of the copper tube which connects the porous cup with the air trap. Certain kinds of rubber tubing become hardened and blackened in contact with the copper. Tubing specified in the drawing has been found comparatively free from this reaction. Coating the outside of the copper with solder, tin, shellac, or bakelite varnish also prevents this trouble. Shellac and varnish will plug or foul the inside of the capillary manometer if allowed to get inside the tensiometer system.

A number of considerations enter in determining the size of the copper tubing used for connecting the porous cup with the air trap. Water can be poured into and will replace air from $\frac{3}{8}$-inch O.D. (0.030-inch wall) copper tubing, whereas smaller diameters require special filling arrangements. On the other hand unnecessarily large diameters increase "thermometer action" of the tensiometer water during the diurnal temperature swing (2). To avoid telescoping and breakage, the glass air-trap should have the same outside diameter as the adjoining copper tubing. Using $\frac{3}{8}$-inch copper tubing specified in figure 1 A and B

[4] Manufactured by the General Ceramics Company, Keasbey, New Jersey.

makes it necessary to use special microstoppers (18 mm. high, 12 mm. top diameter, 7 mm. bottom diameter) in the air trap. If $\frac{7}{16}$-inch copper tubing is used, the air traps can be large enough to take No. 00 rubber stoppers, which are commonly available in the laboratory. The air trap can be flared to take the large stopper, but less trouble has been experienced with leaks when the glass is finished with a light fire polishing and the right sized stopper is used.

A bore of 1.5 mm. is recommended for the capillary glass manometer tube. With a smaller bore it is difficult to avoid errors unless considerable care is used to keep the manometers and the mercury clean; a larger bore decreases sensitivity. A mercury column rising in the manometer will be broken by intervening sections of air or water if the glass capillary is allowed to rest squarely in contact with the bottom of the mercury pot. This may be prevented as shown in the figures by boring out the mercury cavity with a twist drill so as to leave a sloping bottom in the mercury pot. Mercury pots made from 1-inch maple dowel and boiled in paraffin are satisfactory; plastics such as lucite have also been used.

Copper tubing (0.095-inch O.D., 0.040-inch I.D.) is flexible and convenient to use for the water connection at the top of the manometer. A 48-inch length of this tubing is required for the tensiometer shown in figure 1 A and B. It is desirable for added strength to wrap the small tubing as shown in B if the joint to the $\frac{3}{8}$-inch tubing is made with soft solder. If the end of the small tube extends appreciably into the large copper tube the free transit of air and water through the latter will be impeded. The diameter of the small tube is increased to the diameter of the glass capillary by soldering on a $\frac{3}{4}$-inch length of $\frac{1}{4}$-inch O.D. brass or copper tubing.

Rubber, when exposed in the field, weather-checks unless protected from sunlight. The Koroseal tubing[5] used for making the connection at the top of the glass capillary is virtually unaffected by sunlight and is considerably less pervious to gas than is rubber. This material is a thermoplastic and should be heated in boiling water at the time the connection is made.

The aluminum sunshield is worthwhile for protecting the air trap stoppers from the action of sunlight. Wood caps made by boring out maple dowels are equally satisfactory for this purpose. Phosphor-bronz clips retain the glass capillary tube and manometer scale in the channel iron support and also hold the small copper tube against the outside edge of the channel, as shown in figure 1 A.

Holes for the installation of these tensiometers in soil can be made with the standard sized King-tube. Field installations have been made to depths of 15 feet. Since the units can be completely assembled, tested, and have the scale zeros set in the laboratory, the task of field installation consists simply in setting the unit in a King-tube hole in the soil, packing the surface soil around the unit with a $\frac{1}{4}$-inch iron rod, and filling with boiled hot water. A recent

[5] In case Koroseal tubing is not available, the following kind of rubber tubing has been found almost as satisfactory: No. RG 001—$\frac{1}{8}$-inch bore, $\frac{1}{32}$-inch wall. Redman Scientific Company, Los Angeles, California.

installation of 36 units at depths ranging from 6 inches to 5 feet was made by two men in less than two hours.

TENSIOMETER WITH SMALL CUP

It is sometimes desirable to use tensiometers where soil space is restricted or where a minimum of soil disturbance is desired. The gasket-seal tensiometer cup shown in figure 1 C and in detail in figure 1 D and E was designed for such

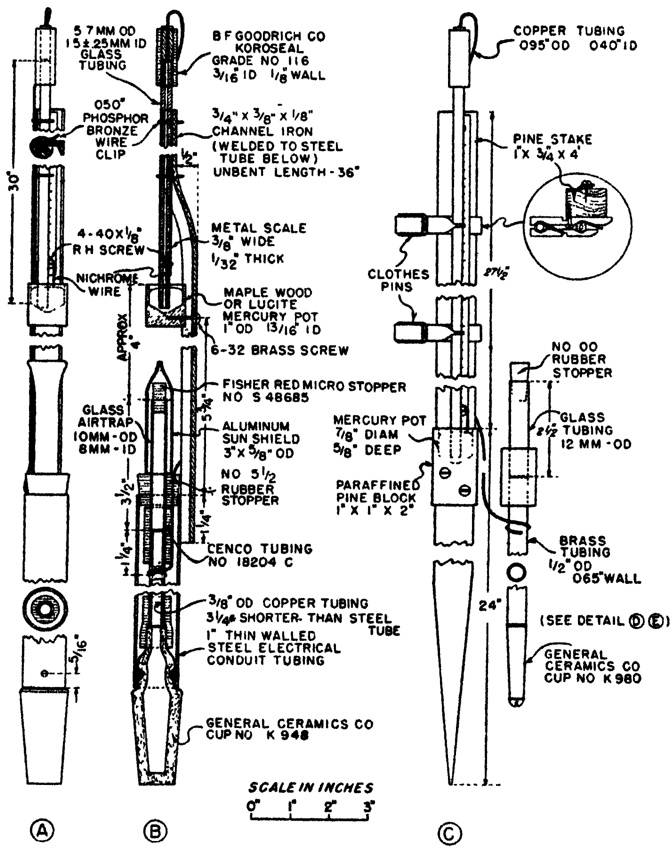

FIG. 1. A AND B, TENSIOMETER FOR FIELD INSTALLATION; C, GASKET-SEAL TENSIOMETER CUP FOR USE IN RESTRICTED SOIL SPACE; D AND E, DETAILS OF GASKET-SEAL CUP FITTINGS; F, TENSIOMETER FITTED WITH BOURDON GAGE

use. A hole for inserting these units can be made by a properly pointed steel pin. The gaskets may be cut on a lathe from Koroseal tubing, and no particular trouble is experienced in obtaining a vacuum seal if the holding screw is gently tightened when the cup and gaskets are boiling hot. The ends of the cup should be smoothed on fine sandpaper or an emery wheel. The flexibility of the gaskets makes this cup mounting surprisingly rugged, and no trouble has been experienced with breakage during installation. Care must be exercised to keep the

opening at the lower end of the glass capillary off the bottom of the mercury pot, because if breaks occur in the mercury column, mercury may be sucked over into the porous cup and will eventually disintegrate the brass fittings.

The wooden stake manometer support shown in figure 1 C may be used in place of the channel iron support shown in A and B.

When precise readings are not required, a Bourdon gage may be substituted for the mercury manometer. Such a tensiometer is shown in figure 1 F. The arrangement of the porous cup and steel tube is the same as that shown in figure 1

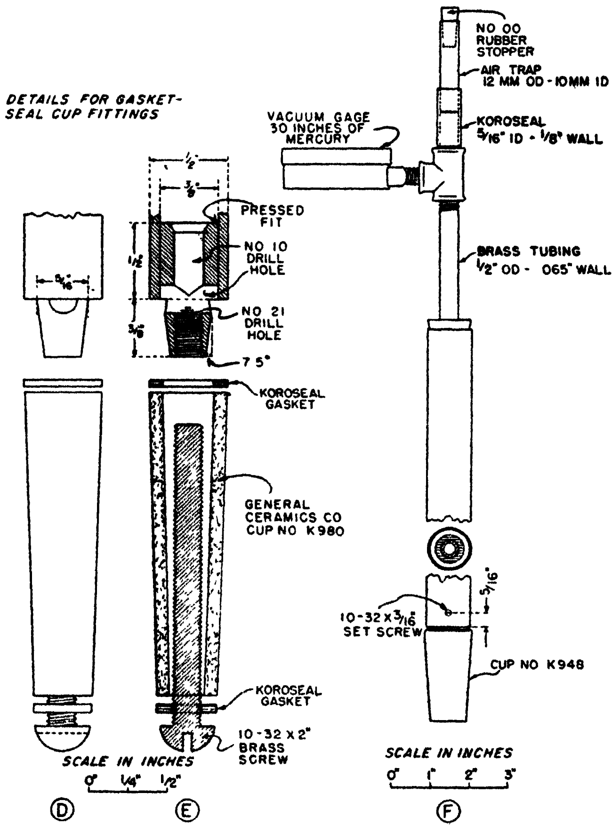

FIG. 1. (*Continued*)

A and B. On such units the air trap stopper should be inserted slowly so as not to damage the vacuum gage.

FILLING AND TESTING

All tensiometers should be tested for air leaks before being put in service. A single-piece ear syringe with a soft rubber pointed spout may be conveniently used for filling tensiometers with hot distilled water.[6] The syringe should be

[6] Distilled water should be used in testing work so that the water conductance of the porous cup will not be impaired by evaporation deposits. Distilled water is unnecessary when the cup is in the soil.

inserted in the air trap and water forced up the small copper tube and out past the mercury in the pot. By use of an aspirator or by mouth the mercury column should then be pulled up several times and suddenly released so as to remove air from the glass-to-metal junction at the top of the manometer.

The following are two procedures that may be used to test for leaks: 1. Pull the mercury column up by applying suction at the air trap and clamp off. The mercury meniscus in the capillary should remain 65 cm. or more above the mercury pot. The water in the tensiometer must be allowed to cool and excess water must be removed from the outer surface of the porous cup before a column this high can be maintained. 2. Completely fill the tensiometer with boiling water as above and insert the rubber stopper in the air trap. The mercury column will then begin to rise if evaporation is allowed to take place from the surface of the porous cup. This evaporation may be accelerated by use of an electric fan. The mercury meniscus in the manometer should rise at least 65 cm. above the mercury in the reservoir and remain above this point while the water disappears from the air trap. With either of these methods it is likely that air absorbed on the inner surfaces of the tensiometer will collect in the air trap and will have to be replaced once or twice with boiled water before the required test pressure can be attained.

MANOMETER SCALES AND ZERO SETTINGS

Ordinarily when the manometer scale on a tensiometer is read, either the negative pressure or the hydraulic head (3, 4) of the cup water is wanted. These are usually expressed in mercury-column or water-column units. Since a counterbalancing water column comes into action as the mercury column rises in the capillary, the "effective" density of the mercury in the manometer is 12.5 instead of 13.5 (3). To simplify reduction of the measurements the writer has used manometer scales which are graduated in special units. On one scale, units were 8 per cent longer than centimeters and were divided in tenths. This scale, when used on manometers like those shown in figure 1 A, B, and C, corrects for the counterbalancing effect of the water and indicates changes in cup-water tension directly in centimeters of mercury. The other type of scale is calibrated to read cup-water tension directly in centimeters of water. The main divisions on this scale are 0.8 cm. apart, each corresponding to 10 cm. of water, with five subdivisions, each corresponding to 2 cm. of water. Both of these scales were made on nickel-silver stock $\frac{1}{32}$ x $\frac{3}{8}$ x $27\frac{1}{2}$ inches.[7] Inexpensive inch or centimeter scales, of course, may be used (2).

There is advantage in using water-column units whenever hydraulic head and hydraulic gradient are being considered in relation to soil moisture movement. Also, centimeters of water are the units commonly used for plotting sorption curves showing the relation between soil moisture tension and moisture content.

The elevation of the zero point of a manometer scale must be definitely located with respect to the mercury surface in the pot if correct readings are to be

[7] These scales were made by the Kennedy Name Plate Company, 4509 Pacific Blvd., Los Angeles, California.

obtained. The displacement of the zero point is required to compensate for the capillary depression of the mercury meniscus in the glass manometer tube and for the pressure change occurring in the water column which extends from the meniscus to the porous cup. A piece of 18-gage Nichrome or Chromel wire fastened to the lower end of the metal scale by a 4–40 x $\frac{1}{8}$-inch screw has been used for the zero indicator.

The elevation that the scale zero must have above the mercury pot for correct reading of cup-water tension may be determined by adjusting the scale so that the mercury meniscus in the manometer tube comes opposite the correct reading on the scale for any given and known cup-water tension. It is important to have a tensiometer completely filled with water before the zero position of the scale is determined. With assembled tensiometers like figure 1 A, distance from the scale zero to the end of the index wire is equal to the equilibrium mercury-column reading when the porous cup is half immersed in a vessel of water. A more generally usable procedure for determining the length of the scale zero-index wire is to leave out the air-trap stopper after the tensiometer is installed in the soil and filled with water. Under this condition the cup-water tension is negative (pressure is greater than atmospheric pressure) and equal to the hydrostatic pressure of the water column extending from the air-trap opening to the center of the porous cup. The scale zero, therefore, should stand above the manometer meniscus by the number of scale units corresponding to this water column. In other words, the correct length for the zero-index wire is equal to the elevation of the manometer meniscus above the mercury surface in the pot with the air trap stopper out plus the number of scale units equivalent to the vertical water column extending from the air trap opening to the porous cup.

The manometer scale can be set to read directly the hydraulic head of the cup water using the soil surface as the reference datum (3, 5). In this case, the length of the scale zero-index wire is equal to the elevation of the manometer meniscus above the mercury surface in the pot with the air trap stopper out plus the number of scale units equivalent to the water column extending from the air trap opening to the soil surface. When the length of the index wire is once properly determined, the elevation of the manometer scale should be adjusted before each reading so that the end of the index wire just touches the mercury surface in the pot.

USE AND LIMITATIONS OF TENSIOMETERS

In the one-atmosphere soil moisture tension range, tensiometers provide direct information on the security with which water is held by soil, on whether the moisture content is increasing or decreasing, and on the direction of movement of soil moisture. Before tensiometer data can be used for determining the actual amount of moisture stored in or removed from the soil, or for determining the rate of moisture flow, it is necessary to have information on the way in which both the moisture content and the permeability are related to the soil moisture tension.

Even though tensiometers will not operate successfully over the whole soil-

moisture range that will permit the growth of plants, field experience indicates that they are useful for indicating the depth and rate of penetration of water in soil and for indicating the comparative rate at which moisture is extracted from soil at various depths. They appear also to have definite usefulness for studying and controlling moisture movement in connection with irrigation, and have been found to stay on scale throughout the year at moisture contents found under commercial irrigation practice for some crops.

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THE CHEMICAL COMPOSITION OF THE CLAY FRACTIONS OF THE BLACK PRAIRIE SOILS OF MINNESOTA[1]

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The general factors involved in the formation of soils and influencing the composition of the weathering products, the clay and colloidal material, are age and kind of parent material, topography, climate, and vegetation, and the length of time over which these factors have been operative. Different types of soils arise from the variable influence of these factors, the dominant effect of one or two over the others producing differences that are reflected in the soil profile. Recognition of these facts led Marbut (15) to apply and modify the system of classification of the Russian pedologists to American soils and separate them into soil zones. Thus did Marbut set up a zone of black prairie soils. In Minnesota these soils cover a roughly triangular area approximately 200 miles across in the southern part of the state and extending north to terminate in a peak in west central Minnesota (15, pl. 2). The parent material consists of deposits laid down during several different glacial periods. The native vegetation was long prairie grasses, the topography is nearly level to rolling, and the precipitation varies from 26 inches in the western part of the zone to 32 inches in the eastern part.

The present work consists of a study of the clay fractions separated from representative black prairie soils of southern Minnesota and from a chernozem and a gray-brown podzolic profile, types of soils that border the prairie soils on the west and east respectively. Though it is recognized that definite conclusions cannot be drawn from a comparison of only one chernozem and one gray-brown podzolic soil with the prairie soils, some information can be gathered on the relative effect of the weathering processes in these soils as reflected by a chemical analysis of the clay fractions. Information is also sought on whether the black prairie soils of Minnesota are a zone of transition between the chernozem and brown podzolic soils, both of which are characterized by definite morphological features, or whether the black prairie soils have characteristics sufficiently different from those of adjacent soils to warrant their classification as zonal soils.

REVIEW OF LITERATURE

Among the earliest analyses of colloidal material reported in the literature is that of Schloesing (22) who analyzed the fine material remaining in suspension for 37 days from several kaolins and concluded that this colloidal matter was

[1] Paper No. 1932 of the Scientific Journal Series, Minnesota Agricultural Experiment Station.

[2] Instructor of soils, University of Saskatchewan, and professor of soils, University of Minnesota, respectively.

not exactly of the composition of kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) though it was considered to be a hydrous aluminum silicate.

Robinson and Holmes (21) in their study of the chemical composition of soil colloids compiled a table of the analyses of clays as reported up to 1924 by soil chemists and ceramists. This table showed that the fine soil fractions were composed chiefly of silica, alumina, combined water, or an unduly large proportion of organic matter, and generally iron oxide. From the data derived by Robinson and Holmes from the results of their work, it was concluded that in general the colloidal matter developed in dry regions was higher in silica, calcium, and sodium than were colloids developed in humid regions. The average silica-sesquioxide ratio for the colloidal fraction of the black prairie soil examined was 2.90 and for the gray-brown podzolic, 2.58.

The analyses and ratios of chernozem, black prairie, and gray-brown podzolic profiles indicated to Byers and Anderson (9, 10) and to Brown and Byers (6) a close relation between the black prairie soils and chernozems, as shown by the silica-sesquioxide, silica-alumina, and silica-iron oxide ratios. Appreciable fractionation of the aluminosilicate had not occurred in the prairie soils, but slight podzolization had, as the silica-iron oxide ratios indicated.

A comparison of the various ratios calculated from chemical analysis of soil colloids from black prairie and chernozem soils was also reported by Middleton, Slater, and Byers (16). The colloid composition of Colby silt loam was uniform and was characterized by high ratios. Shelby silt loam had an unweathered profile with uniform colloid composition and showed no evidence of podzolization. Slight but distinct podzolization was shown in Marshall silt loam, whereas in Palouse silt loam considerable podzolization had occurred.

Reifenberg and Adler (19) separated the colloids from soils by means of a cataphoretic technique. The constituents and ratios as they determined them were compared with analyses reported by American workers on colloids separated by the supercentrifuge from similar soil types. The silica-sesquioxide ratios of a chernozem and two black prairie soil colloids extracted by cataphoretic means were 3.58, 3.44, and 2.71, compared with 3.34, 2.75, and 2.82 for similar soil colloids extracted by the centrifuge method.

In the study of claypan soils, Brown, Rice, and Byers (7) investigated the colloids extracted from four chernozems, a chestnut-brown soil, two solonetz soils, and a prairie soil. Some podzolization was reflected in the prairie soils by the ratios of silica to iron oxide and of iron oxide to alumina. Fractionation of the colloid had occurred and resulted in some accumulation of iron in the B_2 horizon as indicated by the decreased ratio of silica to iron oxide and by the increased ratio of oxide to alumina. A ratio of silica to total base exceeding that of the chernozems indicated greater leaching of bases in the prairie soil.

The properties of colloids from dry-land soils (ten pedocals) were discussed by Brown and Byers (8). The colloid throughout the profile was found to be very constant in composition and in physical properties.

Morosow (18) investigated the physical and chemical properties of the clay fraction, particles less than 1μ in size, of separate genetic horizons of three podzols and two meadow-podzol soils. This author found that the general

composition of all clay fractions was similar, independent of the genetic horizon from which the clay fraction had been separated.

Robinson (20) analyzed the clay fraction, less than 2.0μ, from 28 podzolized soils in North Wales, and found the silica-sesquioxide ratio to be 1.85 and the silica-alumina ratio to be 2.40.

Among others, analyses of soil colloidal material have been reported by Bray (5), Holmes (12), Holmes and Edginton (13), Bradfield (4), Baver and Scarseth (2) and Kelley, Dore, and Page (14).

MATERIALS AND METHODS

Soils studied

The soil samples used in this study were collected from nine profiles located at approximately 20-mile intervals on a line about 30 miles north of and almost parallel to the southern border of Minnesota. The most westerly, profile 1, a representative of the Barnes series, was a typical chernozem. To the east of this, seven profiles, 2 to 8 inclusive, of black prairie soils were sampled, and to the east of these, one profile, 9, of a gray-brown podzolic soil. Of the seven black prairie profiles the most westerly five were of the Clarion series, and the two to the east, of the Carrington series. The gray-brown podzolic soil is a representative of the Lindley series.

The chernozem was developed on Iowan drift, a calcareous glacial till, overlain by a thin covering, no more than a few inches, of loessial material. The five profiles of black prairie soil of the Clarion series were developed on Late Wisconsin drift, a calcareous glacial till, and the two from the Carrington, on Iowan drift. The gray-brown podzolic soil also formed on Iowan drift. The Late Wisconsin drift was a later deposit than that of the Iowan drift; therefore on the latter, more mature soils would be expected.

The black prairie profiles were all very similar in texture. The A horizons varied from heavy loams to clay loams with silt loams predominating. The B and C horizons were silt loams, silty clay loams, or clay loams. The color of the surface soil varied from dark brown to black. The B and C horizons of most samples were light brown. Organic matter and nitrogen contents were high in the surface, becoming progressively less with depth.

The reaction of the profiles was generally acid, but only mildly so, with a pH of 6.23 in the surface of the profile farthest west, to a pH of 5.10 in the surface of the profile farthest east. When each profile was considered as a unit, total exchangeable bases were found to decrease from west to east. This decrease in bases and increase in acidity from west to east, indicated an increase in leaching.

The surface of the Barnes chernozem was dark grayish brown, growing lighter in color with depth in the profile. The A and B horizons were clay loams, the C horizon, a silt loam. The B_2 horizon was a very definite zone of lime accumulation, characteristic of chernozem soils.

The gray-brown podzolic profile had a dark brown surface, shading to gray at intermediate depths, with brown coming in again at lower depths due to sand. The texture of the soil varied from silt loam in the upper horizons to clay loam

and sandy loam at lower depths. Podzolization was evident in the 5–8-inch depth, in the light gray color and weakly lamellar structure, resulting from extensive leaching and acid conditions.

Method of extraction and size of particles separated

The method used in this study for the separation of the clay fraction was essentially that described by Moore, Fry, and Middleton (17), Bradfield (3), and Holmes and Edgington (13).

The procedure was as follows: 300 gm. of soil was rubbed and agitated by hand in about 4 gallons of distilled water. No dispersing agent was employed. The suspension was transferred to a large container and further agitated by means of a mechanical stirrer for about 20 minutes. After settling for a further 20 minutes the suspension was drawn off and passed through a Sharples supercentrifuge exerting a force of about 20,000 times gravity. The colloidal material passing through the centrifuge was then concentrated by means of Pasteur-Chamberlain filters. The filtrate sucked off was used again for further dispersion of the soil, and the entire procedure was repeated until virtually all the colloid had been removed from the soil. The clay fractions concentrated on the filters were finally rubbed off, a limited amount of water being used, and were evaporated to dryness on the steam bath. Examination under the microscope showed that 2μ was the upper limit of size of particle separated from soil by the method of extraction used.

Methods of analysis

Methods commonly employed in the analysis of soils and silicate rocks were used.

The method for determining soluble silica, as yet unpublished, was developed in these laboratories by Rost and Maehl and is as follows: weigh out ½ gm. of colloid, add 25 ml. of 1 per cent HCl, and allow to stand for 3 hours with occasional stirring. Filter and digest the filtered soil on the steam bath in 50 ml. of 5 per cent KOH for 1½ hours, stirring now and then. Filter and acidify the filtrate with HCl. Evaporate to dryness on the steam bath, then further heat in the oven for 1 hour at 110–115°C. Cool and take up with 10 ml. of 1:1 HCl, filter and wash with 1:100 HCl. Ignite the material on the filter paper in a weighed platinum crucible, cool, and weigh. Add 2 or 3 drops of dilute H_2SO_4 then 5 ml. of HF and evaporate to dryness. Ignite with the full flame of the Bunsen burner, cool, and weigh. The difference in weight between the ignited silica and impurities and the hydrofluorized residue represents the "soluble silica" in the sample. The running of blanks with each batch of samples is essential, particularly if the digestion with KOH is done in porcelain or pyrex vessels.

RESULTS

Chemical analysis of the clay fractions

The chemical analysis of the clay fractions extracted from the profile samples from the various soil zones are presented in table 1. Loss on ignition and organic

TABLE 1

Chemical analysis of the clay fractions from chernozem, black prairie, and gray-brown podzolic soils

Results in percentages

PROFILE NUMBER AND HORIZON	LOSS ON IGNITION	ORGANIC MATTER*	COMBINED WATER	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	P_2O_5	CaO	MgO	K_2O	Na_2O
Chernozem												
1-A	21.36	11.81	9.55	54.19	11.49	25.44	0.46	0.31	1.90	2.74	2.72	0.03
B_1	14.72	7.57	7.15	56.07	11.60	24.46	0.48	0.12	1.89	2.74	2.45	0.03
B_2	13.26	7.08	6.18	55.88	11.41	24.12	0.50	0.09	2.40	2.85	2.56	0.02
C	13.17	6.96	6.21	56.62	11.24	23.36	0.46	0.12	2.48	2.90	2.69	0.02
Black prairie												
2-A	22.24	10.89	11.35	53.78	12.64	25.58	0.33	0.52	1.85	2.53	2.55	0.02
B_1	18.55	8.97	9.58	54.53	12.50	25.29	0.39	0.34	1.92	2.73	2.32	0.01
B_2	13.66	4.73	8.93	54.30	13.00	25.00	0.37	0.24	2.46	2.59	2.17	0.01
3-A	24.83	12.76	12.07	53.23	13.95	25.65	0.43	0.41	1.81	2.46	2.46	0.02
B_1	20.86	10.91	9.95	53.13	13.75	25.74	0.45	0.35	1.72	2.74	2.52	0.01
B_2	19.80	9.48	10.32	53.52	14.20	25.64	0.35	0.26	1.45	2.57	2.12	0.01
4-A	28.63	14.57	14.06	53.15	14.51	22.60	0.54	0.83	2.36	2.60	2.78	0.02
B_1	21.80	11.29	10.51	54.12	14.44	23.64	0.47	0.58	1.89	2.59	2.26	0.01
B_2	16.61	9.15	7.46	54.92	14.87	22.64	0.45	0.49	1.81	2.68	1.99	0.01
5-A	22.70	11.84	10.86	52.53	14.63	22.55	0.50	0.43	3.76	2.37	2.42	0.02
B_1	18.20	9.31	8.89	55.84	13.48	23.41	0.45	0.20	1.97	2.54	2.16	0.02
B_2	14.96	6.97	7.99	54.99	14.60	22.83	0.46	0.16	1.74	2.61	2.11	0.01
C	11.43	4.06	7.37	57.40	14.49	20.82	0.47	0.17	1.72	2.77	1.93	0.01
6-A	26.82	14.10	12.72	55.93	11.90	22.31	0.53	0.94	2.43	2.64	2.62	0.01
B_1	21.96	11.43	10.53	55.73	11.65	23.46	0.55	0.74	1.72	2.96	2.37	0.01
B_2	16.78	7.72	9.06	56.79	12.43	22.95	0.53	0.50	1.72	2.86	2.34	0.01
7-A	16.74	9.22	7.52	50.69	13.76	27.38	0.54	0.53	1.28	2.44	2.42	0.01
B_1	15.82	8.10	7.72	51.78	13.77	26.75	0.55	0.44	1.51	2.63	2.36	0.01
B_2	13.62	5.94	7.68	52.26	15.19	25.64	0.49	0.35	1.53	2.63	2.20	0.01
C	11.91	2.91	9.00	50.03	15.78	27.06	0.43	0.41	1.29	2.31	2.26	0.01
8-A	26.60	15.40	11.20	50.19	14.82	26.01	0.65	0.92	1.83	2.42	2.61	0.02
B_1	22.44	11.31	11.13	50.84	15.67	25.30	0.59	0.78	1.82	2.38	2.47	0.01
B_2	17.34	9.51	7.83	51.48	16.24	24.74	0.55	0.61	1.44	2.38	2.12	0.01
Gray-brown podzolic												
9-A	24.99	11.86	13.13	50.79	13.23	27.54	0.53	1.23	1.53	2.76	1.95	0.02
B_1	17.13	7.23	9.90	52.79	13.50	26.94	0.53	0.71	1.23	2.57	1.84	0.02
B_2	16.76	7.00	9.76	49.76	17.21	26.42	0.45	0.67	1.25	2.43	1.84	0.01

* Calculated from organic carbon.

matter (and thus combined water also, which represents the difference between the two) have been calculated on the basis of the oven-dry weight less the ignition loss. In this way differences or similarities in the inorganic constituents can be shown without being obscured by variable amounts of organic matter and combined water.

Loss on ignition represents chiefly the combustion of organic matter plus the loss of combined water and water of hydration. No consistent trend is to be found between the profiles. The loss from the surface horizons of the black prairie profiles varies from 16.74 per cent to 28.63 per cent, with the least loss in the horizon of profiles 5 and 7. In all profiles the greatest loss is in the surface horizon, and the loss decreases from the surface downward.

No trend of organic matter is apparent between profiles, the only consistent relation being within the profile itself, namely, a decrease in organic matter content with depth. In these analyses organic carbon was determined and the organic matter has been calculated on the basis of 58 per cent carbon content using the Wolf factor $0.471 \times CO_2$. In many investigations of fractions of soil organic matter, the carbon content has been found to be much lower than 58 per cent (1). If such has been the case in determining the organic matter in these samples, differences within the profile would be greater than those shown, since the amount of organic matter decreases with depth.

The differences in combined water between and within the profiles are not so great as those of ignition loss or organic matter. Some of the differences between the horizons within the profiles could be accounted for if, as has been mentioned, the organic matter determinations were low, but the differences are probably greater than can be accounted for by this possibility. If organic matter has a greater power than inorganic colloids to combine with water, then it would be expected that the combined water would be greater in upper horizons where the amount of organic matter is the greatest.

In the solum proper of each soil profile, the fairly constant silica content indicates uniformity of composition of the clay fraction. The profiles as a whole, compared one with another, show pronounced differences, and on the basis of silica content, they can be divided into two groups. The silica content of profiles 1 to 6 varies approximately from 53 to 56 per cent. Earlier in this paper it was pointed out that the samples representing the Barnes series (profile 1), the Carrington series (profiles 7 and 8) and the Lindley series (profile 9) were developed on Iowan drift, whereas the Clarion series (profiles 2 to 6 inclusive) were developed on Late Wisconsin drift, a more recent geological deposit. This difference in age and parent material could account for the differences in silica content. It is logical to assume that profiles 7, 8, and 9 are more mature than profiles 2 to 6, and that longer exposure to climatic factors has caused a greater loss of silica. Some of the difference could be due to the nature of the parent materials, which originally may have differed by 2 or 3 per cent in silica content.

On the basis of silica content alone, it is not possible to distinguish the black prairie soils from either the chernozem or the gray-brown podzolic soils here considered. Differences in the Clarion and Carrington series are evident, however.

In the chernozem profile (number 1) the iron content is remarkably uniform, indicating a very uniform type of clay fraction in all four horizons. There is a slight increase in iron in the B_1 horizon but it is doubtful whether it is great enough to indicate any accumulation at this depth. The iron content of the clay fractions of the black prairie soils is also uniform, on the whole, indicating a fairly constant clay composition. It will be noticed, however, that in every instance there is a small but definite increase in the percentage of iron in the B_2 horizons over that in the B_1. This increase varies from about $\frac{1}{2}$ to over 1 per cent and may be considered significant when it occurs in all of the seven profiles. There is a definite indication here that some iron has been removed from the A and B_1 horizons and deposited in the B_2. Weathering has progressed further on these soils than on the chernozem, resulting in some fractionation of the soil minerals and subsequent transportation downward of decomposition products.

The picture displayed by a definitely podzolic soil is shown in the data for profile 9. A rise in the percentage of iron oxide in the B_2 horizon of over 3 per cent above that found in the B_1 horizon indicates a still more advanced stage of weathering than that found in the black prairie soils. Thus the iron content of the clay fraction of the black prairie soils appears to exhibit characteristics similar to podzolic profiles. Fractionation and decomposition in these soils have been sufficient to be shown by analysis, which is not the case in the chernozem. On the other hand weathering has not progressed so far in the black prairie zone as in the gray-brown podzolic zone.

The alumina content of the clay fractions as shown in table 1 indicates generally a fairly constant colloid composition. In all profiles the alumina content decreases from the B_1 to the B_2 horizon. This might indicate a preferential removal of iron and a slower removal of alumina, giving the appearance of an accumulation in the B_1. This does not hold, however, for profile 1, the chernozem, in which no iron accumulation in the B_2 was evident.

The amount of titanium is fairly uniform within the profile and there are no great differences between the profiles. In three cases the percentage is slightly higher in the A than in the B horizons. Generally the B_2 and C horizons are lower in this constituent than are upper horizons.

The phosphorous content of the samples does not show the uniformity that constituents heretofore discussed have exhibited. In every case the A horizon contains the greatest amount of phosphorous, and the percentage declines steadily from the surface downward in all except profiles 1, 5, and 7, in which there is a rise in the C horizon. The phosphorous content of the clay fraction of the prairie soils varies considerably, but lies intermediate between the chernozem profile, which has the lowest content of phosphorous of all, and the gray-brown podzolic profile, the A horizon of which contains 1.23 per cent of P_2O_5, the highest amount shown. Other investigators (11, 21) found a higher phosphorous content in the colloid than in the whole soil, indicating that phosphorous may be concentrated in the finer fraction of the soil.

The calcium content of the samples is, on the whole, rather high. Leaching in profiles 1 and 2 has not been sufficient to remove calcium beyond the B_2 horizon apparently. Carbon dioxide was not determined in any of the clay

fractions, but it is likely that some colloidal calcium carbonate has been extracted from the B_2 and C horizons of profile 1 and from the B_2 horizon of profile 2, and this could partly account for the high calcium content found. The remaining black prairie profiles, 3 to 8, present a picture more or less intermediate between profiles 1 and 2 and profile 9. The last shows clearly, in its reduced calcium content, the effects of greater leaching that has occurred in a podzolic type of environment.

The amount of magnesium is high in all samples and indicates either one or two possibilities, namely, that there is present in the clay fraction some mineral or minerals very resistant to hydrolysis, or that the colloid complex present has a very strong affinity for this base. The result may be the effect of both these factors. No differences among any of the profiles are great enough to characterize the chernozem, black prairie, or gray-brown podzolic soils as such.

The potassium as potassium oxide shows some differences both within and between profiles. The black prairie profiles all show an accumulation of potassium in the A horizon and, with the exception of profile 3, there is a gradual

TABLE 2

Percentage soluble silica in the clay fractions from chernozem (profile 1), black prairie (profiles 2 to 8), and gray-brown podzolic (profile 9) soils

HORIZON	PROFILE NUMBER								
	1	2	3	4	5	6	7	8	9
A	6.54	8.00	9.40	8.35	8.60	10.93	9.37	9.21	10.24
B_1	5.86	7.57	7.63	7.90	7.95	10.25	9.53	9.54	9.56
B_2	4.75	6.51	8 23	8.20	8.30	9.83	8.57	9.46	9.54
C	5.65	..	.		8.49	.	7.76	.	

decrease with depth. This is also evident in the gray-brown podzolic profile, though to a lesser degree. The chernozem profile is fairly uniform in potassium, though the A and C horizons have slightly higher percentages then the B. The black prairie profiles, the potassium content of which is very similar, again exhibit an intermediate position between the slightly weathered chernozem profile, on the one hand, and the more highly weathered gray-brown podzolic profile, on the other.

The amount of sodium is very small, indicating extensive removal of this base from all profiles. The content is fairly uniform in all samples, with a slightly higher amount in most upper horizons.

Soluble silica in the clay fractions

The method used for soluble silica is rather an arbitrary one but should yield comparative results. Table 2 presents the percentages of soluble silica in the clay fractions. The results were calculated on the basis of oven-dry weight less loss on ignition, in order to enable comparison of the samples on a strictly inorganic basis.

In seven of the nine profiles the percentage of soluble silica is highest in the A horizon, and in six the percentage is higher in the B_1 than the B_2. Thus, in general, the tendency is for the soluble silica to decrease in amount from the surface downward. It will be noticed also that the percentages in the A horizons are considerably higher in the black prairie and the podzolic soils than in the chernozem. This is further indication that weathering in the black prairie soils has advanced considerably beyond that in the chernozem. There is little difference between the amounts of soluble silica found in profile 9, the gray-brown podzol, and profiles 6, 7, and 8, the black prairie soils that lie closest to it. The variation among all the black prairie soils is slight. This would indicate that the black prairie soils are zonal and that they appear closer to the gray-brown forest soils than to the chernozems.

Derived data

Table 3 presents the various ratios derived from the analytical data. Except for the C horizon of profiles 5 and 7 and the B_2 of profile 9, the silica-sesquioxide ratios indicate considerable uniformity of the clay fractions of these soils. Definite fractionation and decomposition of the soil minerals are indicated only in profile 9, in which the ratio drops from 2.51 in the B_1 horizon to 2.26 in the B_2 horizon, indicating accumulation of sesquioxides, principally iron, as has already been pointed out. An abrupt change in the magnitude of the ratios occurs between profiles 6 and 7. This change must be attributed largely to the differences in age and kind of parent material.

The average silica-sesquioxide ratio for the clay fractions of the A, B_1, and B_2 horizons of the prairie soils is 2.73, intermediate between the chernozem profile, with an average ratio of 2.94, and the gray-brown podzolic profile with an average ratio of 2.39 (table 4).

The silica–iron-oxide ratio of the clay fractions of the chernozem, profile 1, widens with depth in the profile. In the black prairie profiles the ratios are fairly uniform, but consistent, though some small differences are noted. In all profiles except number 8, the ratio is wider in the B_1 horizon than in the A, and in all cases the ratio in the B_2 horizon is narrower than in the B_1. The ratios for the black prairie soils show distinct differences from those exhibited by the chernozem profile. Profile 9, in which podzolization has acted to a greater extent, has the smallest ratio of any horizons analyzed, a ratio of 7.69 in the B_2. This is characteristic of podzolic soils and is a more pronounced example of what has occurred to a lesser extent in the black prairie soils and is not in evidence at all in the chernozem.

The average silica–iron-oxide ratio for the A, B_1, and B_2 horizons of the prairie soils is 10.29, which is intermediate between the chernozem profile with an average ratio of 12.80, and the gray-brown podzolic profile with an average ratio of 9.42 (table 4).

The only profile of the group that shows any indication of an accumulation of aluminum in the B_2 is number 9. The narrowing of the silica-alumina ratio is so slight, however, that its significance is questionable. In the other profiles

TABLE 3

Ratios derived from the analytical data for chernozem, black prairie, and gray-brown podzolic soils

PROFILE NUMBER AND HORIZON	$\frac{SiO_2}{Fe_2O_3 + Al_2O_3}$	$\frac{SiO_2}{Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	$\frac{SiO_2}{\text{TOTAL BASES}}$
Chernozem					
1-A	2.81	12.53	3.62	.288	6 88
B_1	2.98	12.85	3.89	.303	7.28
B_2	3.02	13.02	3.93	.302	6.60
C	3.15	13.40	4.11	.307	6.50
Black prairie					
2-A	2.71	11.32	3.57	.315	7.27
B_1	2 78	11 60	3.66	.316	7.16
B_2	2.77	11.11	3.69	.332	6.88
3-A	2.61	10.15	3 52	.347	7 40
B_1	2 61	10.27	3.50	.341	7.04
B_2	2.62	10.02	3.54	.354	7.94
4-A	2.83	9.74	3.99	.410	6 48
B_1	2.80	9.96	3.89	.390	7.37
B_2	2.90	9 82	4.12	.419	7.62
5-A	2.80	9.55	3.95	.414	5 75
B_1	2.96	11.02	4.05	.368	7.66
B_2	2.90	10.02	4.09	.441	7 74
C	3 24	10.53	4.68	.444	7.96
6-A	3.11	11.60	4.25	.367	6 81
B_1	3.06	12.72	4.03	.317	7.17
B_2	3.12	12.15	4.20	.346	7.47
7-A	2.38	9.79	3.14	.321	7.75
B_1	2.47	10.00	3.29	.329	7.33
B_2	2.51	9.15	3.46	.378	7 49
C	2.29	8.44	3.14	.373	7 98
8-A	2.40	9.00	3.27	.364	6 93
B_1	2.44	8.63	3.41	.395	7.18
B_2	2.49	8.43	3.53	.419	8.00
Gray-brown podzolic					
9-A	2.40	10.21	3.13	.307	7.25
B_1	2.51	10.36	3.31	.320	8.32
B_2	2.26	7.69	3.20	.416	8.12

the general trend is for a gradual widening of the ratio with depth. In the individual profiles, the silica-alumina ratios are very similar and indicate fair uniformity of clay composition.

When the silica-alumina ratios for the A and B horizons are averaged, three of the black prairie soils, profiles 4, 5, and 6, have averages higher, and four, profiles 2, 3, 7, 8, averages considerably lower than the average ratio for the chernozem soil. It is to be noted that the profiles with the ratios higher than that for the chernozem are not adjacent to the chernozem belt but well to the east in about the center of the black prairie zone. Profiles 7, 8, and 9 have almost the same average ratios, indicating a very close similarity in the clay composition and in the total and relative effects of the various factors that have combined in forming the clay complex.

The average silica-alumina ratio for the A, B_1, and B_2 horizons of the black prairie profiles is 3.72, intermediate between that of the chernozem, 3.81, and that of the podzolic soil, of 3.21 (table 4).

The iron-oxide-alumina ratios in profile 1, the chernozem, are more uniform than in any other profile examined. The ratio in horizon A is a little narrower than in horizons B_1, B_2, and C, but there is no indication of an accumulation of iron in the B_2 horizon, or of a preferential removal of iron over aluminum. Profile 2 shows equal removal of iron from the A and B_1 horizons, but a definite deposition of iron in the B_2 horizon. Profiles 3, 4, 5, and 6 show either a greater removal of aluminum than iron from the A or a preferential removal of iron from the B_1, since the ratio in the B_1 horizon is narrower than in the A. In the B_2 horizon the iron-oxide–alumina ratio rises again, as would be expected from the higher iron content found in this horizon. The ratios in profiles 7, 8, and 9 follow the same trend, lowest in the A horizon, then increasing in the B_1 and B_2, and highest in the B_2. The ratio in the B_2 horizon of profile 9 shows the greatest widening over the B_1 of any profile examined, and this again is a characteristic of podzolic profiles.

The differences in the iron-oxide–alumina ratios between the B_1 and B_2 horizons are no greater in the black prairie profiles from the eastern part of the zone than in those from the western part. The movement of iron relative to aluminum does not indicate the black prairie zone to be a transition zone. The weathering forces are essentially equal in magnitude, giving rise to a uniform action on the soil minerals and to equal movement and accumulation of iron in the B_2 horizon.

The ratios of silica to total bases for the horizons within the different profiles do not show the uniformity that ratios for other constituents discussed above have shown. In the majority of the black prairie soils and in the gray-brown podzolic soil, bases brought to the surface and left there by decaying vegetation have resulted in some accumulation and hence a narrower ratio in the A horizon. The chernozem profile and one black prairie profile present a somewhat different picture from that shown by the other profiles. The high content of calcium in horizons B_2 and C of profile 2 is the cause of the narrower ratio in these horizons. The ratio thus decreases with depth in the profile, directly opposite to what occurred in the majority of the other black prairie profiles and the one gray-brown podzolic soil examined.

With respect to base saturation the black prairie profiles would seem to occupy an intermediate position between the chernozem soils and the gray-brown podzolic soils. The average silica–total-base ratio of the A, B_1, and B_2 horizons

of the black prairie soils is 7.26, the average ratio for the chernozem soil is 6.92, and for the podzolic soil, 7.90 (table 4).

DISCUSSION OF RESULTS

In table 4 are compiled the various ratios as they were reported in the literature, and as they were obtained in this laboratory. The figures under the column headed "others" were derived in the following manner: If the silica-sesquioxide ratio for the chernozem is taken as an example, all such ratios available, irrespective of the horizon they represented, were averaged, and the figure 3.36 was obtained. The principal objection to this method is that differences within the profile are not indicated. To make the data obtained in this laboratory comparable to that of other workers the ratios for the A, B_1, and B_2 horizons of each profile were averaged also.

The silica-sesquioxide ratios show distinct differences between the chernozem, black prairie, and gray-brown podzolic soils. The ratio narrows with increased degradation of the soil, the black prairie soils maintaining an intermediate position between the semiarid soils—the chernozems—and the humid soils—the

TABLE 4

Comparison of the ratios derived from analyses of the clay fractions from Minnesota soils with those obtained for similar soils by other investigators

SOIL ZONE	$\frac{SiO_2}{R_2O_3}$		$\frac{SiO_2}{Fe_2O_3}$		$\frac{SiO_2}{Al_2O_3}$		$\frac{Fe_2O_3}{Al_2O_3}$		$\frac{SiO_2}{\text{TOTAL BASES}}$	
	Others	Minn.	Others	Minn.	Others	Minn.	Others	Minn.	Others	Minn.
Chernozem	3.36	2.94	16.71	12.80	4.27	3.81	.256	.298	7 11	6.92
Black prairie	2.80	2.73	13.61	10.29	3.47	3.72	.271	.366	7.78	7 26
Gray-brown podzolic	2.38	2.39	10.65	9.42	2.98	3.21	.282	.348	9.63	7.90

gray-brown podzolic soils. Byers, Alexander, and Holmes (11), pointed out that in the prairie and chernozem colloids particularly, the iron and aluminum are largely associated with the silica and thus the silica-sesquioxide ratio most nearly expresses the composition of the colloidal material. In the podzols, on the other hand, probably only a part of the iron is associated with the silica and aluminum and thus the silica-alumina ratio better expresses the composition of the colloids extracted from these soils.

The silica-iron-oxide ratios follow the same trend as those reported in other analyses of the colloidal fractions of soils. The average ratio for the black prairie soils of Minnesota lies between the ratios for the chernozem and the gray-brown podzolic soils, but is closer to the latter. This should indicate the black prairie profiles to be more like the gray-brown podzolic soil. This same relationship was evident when the iron content and the silica-iron-oxide ratios were studied in previous sections. Evidence of podzolization was apparent in the accumulation of iron and in the narrower silica-iron-oxide ratio in the B_2 horizons.

The trend in the silica-alumina ratios is similar to that obtained by other

investigators, the black prairie soils occupying an intermediate position between the chernozem and podzolic soils. The high average silica-alumina ratios in the clay fraction of the Minnesota soils is due principally to three profiles, 4, 5, and 6. Their average is 4.06, while that of profiles 2, 3, 7, and 8 is 3.47, almost identical with the general average of ratios reported in the literature. The ratios do not approach 2:1, the proportion in which silica and alumina, respectively, occur in kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$).

The iron-alumina ratios for the Minnesota soils are higher than those for other soils and do not show the same trend. The iron-alumina ratios in profiles 4, 5, and 8 are similar and the average of the three is 0.402. The average of the remaining black prairie profiles, 2, 3, 6, and 7, is 0.339. The high ratios would seem to indicate a greater concentration of iron than aluminum in the clay fraction of Minnesota soils compared to that found by other investigators for similar zonal soils.

The ratios of silica to total bases are presented in the last column of the summary table. The ratios for the Minnesota soils approximate those reported in the literature. The differences between the zones are not so great, but the trend is in the same direction, the ratio for black prairie soils lying between those of the chernozem and gray-brown podzolic soils. It is logical to suppose that leaching removes bases more rapidly than silica, and thus the ratio of silica to total bases should indicate the relative extent of the leaching that has taken place in a soil. Though not large, the differences shown by the silica–total-base ratios of the clay fractions of the Minnesota soils are distinct and separate the chernozem, black prairie, and gray-brown podzolic soils into definite groups.

SUMMARY

The clay fractions were separated from samples taken from nine profiles in southern Minnesota. The profiles represented one chernozem, seven black prairie soils, and one gray-brown podzolic soil. The clay fractions were subjected to chemical analyses, from which the ratios of silica to sesquioxide, silica to iron oxide, silica to alumina, iron oxide to alumina, and silica to total base were calculated.

The chemical analysis showed that the clay fractions from any one profile were, on the whole, very uniform in composition. Differences between profiles were evident, and such differences were explained largely on the basis of age and kind of parent material and its mode of deposition.

A concentration of iron in the B_2 horizon of all of the seven black prairie profiles indicated some fractionation of the soil minerals and offered distinct though limited evidence of podzolization. No such accumulation of iron occurred in the one chernozem profile examined. The one gray-brown podzolic profile had a greater accumulation of iron in the B_2 horizon than that found in the same horizon of any other profile.

The higher percentages of soluble silica in the clay fractions of the black prairie and gray-brown podzolic soils were interpreted to mean greater weathering in these soils compared to the chernozem.

The data that could be derived from the analytical results were calculated and compared with the averages obtained by other soils investigators for chernozem, black prairie, and gray-brown podzolic soils. Substantial agreement was observed between the two sets of data, and on the basis of these ratios and other contributing evidence, the analysis of the weathered portion of the soil—the clay and colloidal material—supports the field observations in the conclusion that the black prairie soils can be classed in a separate zone. The characteristics of the prairie soils resemble in some respects those of both a chernozem and a gray-brown podzolic soil, but differences were sufficiently distinct to be significant and warrant the separation of the black prairie soils as a zonal type.

Indication that analysis of the clay and colloidal fraction of a soil may be useful in distinguishing soil series were supplied by the differences in the constituents shown by the soils of the Carrington and the Clarion series.

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FLOCCULATION AND ELECTROKINETIC BEHAVIOR OF TWO DEFERRATED SOIL COLLOIDS[1]

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For the determination of mineralogical composition of soil colloids, the free oxides of iron and aluminum must be removed by some procedure. The deferrated colloidal residues thus obtained differ markedly from the original colloids in certain chemical properties. Deferration, in some respects, is similar to podzolization, in that iron and aluminum are rendered soluble and are removed from the mineral base-exchange complex. It is not logical, however, to apply the findings from a study of the colloidal behavior of the deferrated residues to the original colloids, because the removal of these basoid constituents affects the properties of the colloids. It is the purpose of this study to point out the effects of deferration as they are reflected by changes in the flocculation behavior and electrokinetic potential of the colloidal residues.

In previous contributions dealing with this subject (7, 8), it was shown that the removal of free iron and aluminum oxides from soil colloids reduced their anion adsorptive capacity and lowered their ultimate pH, but did not materially influence their cation exchange properties. That no fundamental alterations in the acidoid portion of soil colloids resulted from deferration was indicated by the similarity in the release, by electrodialysis and salt-exchange methods, of Ca, Mg, and Ba ions from untreated and deferrated cation-saturated colloids.

Variations in the ultimate pH values of the soil colloids associated with varying degrees of removal of free iron oxide were not adequately explained in the previous study (8). Some general observations that were made on the flocculating rates of the untreated and the deferrated colloids during anion adsorption studies indicated that the variations in ultimate pH values associated with the deferrating treatments might be correlated with and explained by corresponding variations in the isoelectric pH values of the colloidal residues. If the deferrated residues show lower isoelectric pH values, then the reductions in ultimate pH with deferration might satisfactorily be elucidated, since a general relationship is known to exist between these two soil properties (6).

EXPERIMENTAL METHODS

For the study reported in this paper, colloids were isolated from the A horizon of Colts Neck loam and the B horizon of Penn silt loam. The locations and sampling sites of the profiles of these two soils have been previously described (8).

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The procedure for obtaining variations in the free iron oxide contents of these colloids was identical with that outlined in a previous contribution (8).

The cataphoresis cell used was of the modified Mattson type (4), with a suitable light source and optical arrangement. The velocities of the colloidal particles are reported in terms of μ/sec./volt/cm., and represent the mean of six determinations in either direction of the cell. The zeta potential associated with the particles, when reported in the tables that follow, was calculated from the migration velocities of the particles by the use of the Debey and Hückel modification of the Helmholtz-Perrin equation (1).

After the isolation of the colloidal particles (0.002 mm. and finer), the colloids were deferrated, electrodialyzed, and then Na-saturated by titration with NaOH to pH 7.0. The colloidal suspensions were then diluted to a concentration of 1 gm. per liter by the use of distilled water that had recently been boiled and cooled. The diluted suspensions were then used in flocculation studies.

The Na-saturated colloid suspensions, in 25-ml. portions, each containing 50 mgm. of the colloid, were placed in test tubes and rapidly mixed with 25-ml. portions of standard solutions of HCl, H_2SO_4 and H_3PO_4, respectively. The mixtures were then transferred to test tubes provided with rubber stoppers. The degrees of flocculation observed after 24 hours were recorded. The tubes were then shaken, and cataphoresis measurements were made. The tubes were later reshaken, and the pH values of the suspensions were determined by the use of a glass-electrode potentiometer system.

EFFECT OF DEFERRATION ON ELECTROKINETIC CHARGE OF H-COLLOIDS

The data in table 1, which are concerned with the degree of removal of free iron oxides from the original soil colloids, are presented as an aid in understanding the effect of deferration on the electrokinetic charge. Treatment A (see table 1) resulted in reducing the total Fe_2O_3 content in the Colts Neck colloid from 32.71 to 13.13 per cent; and in the Penn colloid from 8.54 to 4.96 per cent. Treatment B further reduced the content of total Fe_2O_3 to 4.44 per cent in the Colts Neck colloid, and to 3.58 per cent in the Penn colloid. The iron remaining in the colloids after treatment B, is apparently only that which exists in the form of silicates.

The data in table 1 do not give a complete picture of the removal of another important basoid, aluminum, which undoubtedly plays an important role in the flocculation and electrokinetic properties of the deferrated colloidal residues. Table 2 contains data showing the percentage removal of the basoids, iron and aluminum, and of the acidoid, silica, from the colloids. The loss of these constituents from the colloid is the result of the action of the dilute acid digestion of the black Fe_2S precipitate in the Drosdoff method (2) and the release of the forenamed constituents from the colloids during electrodialysis. The Colts Neck colloid, after treatment B, had lost 86 per cent of its total Fe_2O_3 and 27.5 per cent of its total Al_2O_3. By the same treatment, the Penn colloid had lost 58.1 per cent of its total Fe_2O_3 and only 8.5 per cent of its total Al_2O_3.

The removal of the basoids by deferration and electrodialysis is stressed be-

cause, theoretically, the colloidal residues resulting from these treatments should possess higher electronegative potentials than those exhibited by the untreated colloids. This is because of the removal of Fe and Al and the development of a higher SiO_2/R_2O_3 ratio (see table 1). The data support the

TABLE 1

Some chemical properties of untreated and deferrated Colts Neck and Penn colloids

COLLOID	SiO_2/R_2O_3			Untreated Colloid			FREE Fe_2O_3 CONTENT REMOVED BY TREATMENTS	
	Untreated	Residue "A"*	Residue "B"†	SiO_2	Fe_2O_3	Al_2O_3	A	B
				per cent	*per cent*	*per cent*	*per cent*	*per cent*
Colts Neck	1.11	1.57	2.35	26.49	32.71	19.25	19.58	28.27
Penn	2.26	2.40	2.58	45.05	8.54	28.31	3 58	4.96

* No preliminary digestion with a 2 5 per cent solution of Na_2CO_3.
† Preliminary digestion with a 2.5 per cent solution of Na_2CO_3.

TABLE 2

Part of total iron and aluminum oxides and silica removed from Colts Neck and Penn colloids by deferration treatments

COLLOID	TREATMENT	CONSTITUENTS REMOVED BY TREATMENTS		
		SiO_2	Free Fe_2O_3	Al_2O_3
		per cent	*per cent*	*per cent*
Colts Neck	A	3.4	59.8	trace
Penn	A	1.2	41.9	trace
Colts Neck	B	9.5	86.4	27.5
Penn	B	4.7	58.1	8.5

TABLE 3

Relation between degree of deferration and electrokinetic charge of H-Colts Neck and Penn colloids

COLLOID	TREATMENT	MIGRATION VELOCITY	ZETA POTENTIAL
		μ/sec./volt/cm.	*millivolts*
Colts Neck	None	−1.03	−21.6
	A	−1.32	−27 7
	B	−1.39	−29.2
Penn	None	−1.50	−31.5
	A	−1.64	−34.4
	B	−1.93	−40.5

theory. The electronegative potentials of the colloids were increased by deferration, the increases depending upon the degree of basoid removal (see table 3). The cataphoretic charge associated with the original electrodialyzed Colts Neck colloid was −21.6 millivolts, whereas with the deferrated colloidal

residues produced by treatments A and B, and designated as "A" and "B" it was −27.7 and −29.2 millivolts, respectively. The original electrodialyzed Penn colloid, having a higher SiO_2/R_2O_3 ratio than the Colts Neck colloid, had a higher initial cataphoretic charge (−31.5 millivolts) than the latter. Correspondingly, deferration by treatments A and B increased the electrokinetic charge to −34.4 and −40.5 millivolts, respectively.

ELECTROKINETICS AND FLOCCULATION OF DEFERRATED COLLOIDS BY ACIDS

The concentration of HCl, H_2SO_4, and H_3PO_4 required for flocculation, and the electrokinetic behavior of the original and deferrated colloidal particles of Na-saturated Colts Neck and Penn colloids, are presented in tables 4 and 5.

The higher migration velocities of the Na-colloids, when compared with those of the electrodialyzed samples, are explained by the greater dissociation of Na ions from the clay surfaces, and the resulting increase in the cataphoretic potential (5). Data on the migration velocities and the degree of flocculation of the original and progressively deferrated Colts Neck colloid by HCl, are very interesting. Although flocculation of both the original and the deferrated colloidal systems occurred at HCl concentrations of 0.50 m.e. per liter, the charge associated with the flocculated particles seemed to be largely dependent upon the degree of basoid removal from the colloids. This is shown by the higher migration velocities of the deferrated particles. The original Colts Neck colloid was isoelectric, in the HCl system, at pH 3.55, whereas the particles resulting from treatments A and B were strictly electronegative at pH values as low as 2.60. The increase in electrokinetic potential with deferration can be explained if the following facts having to do with the cataphoretic properties of untreated soil colloids are kept in mind.

Soil colloids are amphoteric in nature (6), and the electrokinetic charge associated with their particles is a function of their SiO_2/R_2O_3 ratio or, more logically, of the activity of their acidoid/basoid ratio (3, 6). During the neutralization or suppression of their zeta potential by acids, it is the Donnan distribution of ions that plays the principal role in the process (4). It is a relatively simple process to render colloids of a low SiO_2/R_2O_3 ratio isoelectric, or even electropositive, with dilute acids (3, 4), but this procedure is not very successful when applied to colloids of a high silica/sesquioxide ratio. This is because the activity of the basoid fraction in the high-ratio colloids is at a minimum. Essentially, therefore, the process of deferration is analogous to the soil-forming processes involved in the production of colloids of a high SiO_2/R_2O_3 ratio. The residues resulting from deferration of the original colloids, therefore, exhibit electrokinetic properties, during flocculation by acids, that are similar to those exhibited by colloids of a high SiO_2/R_2O_3 ratio.

The flocculation of the Colts Neck colloid by H_2SO_4 was also of interest. Flocculation was complete in the untreated and A systems at 0.5 m.e. of acid per liter and at some concentration between 0.5 and 0.75 m.e. of acid per liter in the deferrated B residues. Unlike the HCl system, the original colloid was never rendered isoelectric by H_2SO_4. This is probably explained by the formation of a

sulfated soil-colloid complex which is exceedingly difficult to render isoelectric (4). At equivalent acid concentrations, the migration velocities of the flocculated particles in the H_2SO_4 system were generally higher than in the HCl

TABLE 4

Flocculation of Na-saturated Colts Neck colloid by HCl, H_2SO_4, and H_3PO_4, and associated electrokinetic values

CONCENTRATION OF ACID	HCl			H_2SO_4			H_3PO_4		
	Flocculation*	Migration Velocity	pH	Flocculation*	Migration Velocity	pH	Flocculation*	Migration Velocity	pH
m.e./l.		*μ/sec./volt/cm.*			*μ/sec./volt/cm.*			*μ/sec./volt/cm.*	
Untreated colloids†									
0.00	0	−1.77	6.45	0	−1.77	6.45	0	−1.77	6.45
0.50	xxxx	−0.10	3.65	xxxx	−0.20	3.65	0	−0.71	4.20
0.75	xxxx	0 00	3.55	xxxx	−0.16	3.40	xx	−0.43	4.05
1.00	xxxx	+0.07	3.25	xxxx	−0.11	3.20	xxx	−0.31	3.95
1.50	xxxx	+0.11	3.00	xxxx	slow	3.05	xxxx	−0.29	3.65
2.00	xxxx	+0.13	2.85	xxxx	slow	2.90	xxxx	−0.27	3.35
3.00	xxxx	+0.17	2.65	xxxx	slow	2.70	xxxx	−0.25	3.20
Residue "A"									
0 00	0	−2.00	6.45	0	−2.00	6.45	0	−2.00	6.45
0.50	xxxx	−0.27	3.50	xxxx	−0.37	3.70	0	−1.09	4.15
0.75	xxxx	−0.26	3.40	xxxx	−0.27	3.35	x	−0.47	3.90
1.00	xxxx	−0.16	3.15	xxxx	−0.21	3.05	xx	−0.40	3.70
1.50	xxxx	−slow	2.95	xxxx	−0.20	3.00	xxx	−0.33	3.40
2.00	xxxx	−slow	2.85	xxxx	−0.17	2.70	xxxx	−0.32	3.25
3.00	xxxx	−slow	2.60	xxxx	−0.14	2.70	xxxx	−0.30	3.10
Residue "B"									
0.00	0	−2.42	6.50	0	−2.42	6.50	0	−2.42	6.50
0.50	xxxx	−0.40	3.50	xxx	−0.47	3.60	0	−0.76	4.10
0.75	xxxx	−0.40	3.30	xxxx	−0.37	3.35	0	−0.58	3.80
1.00	xxxx	−0.34	3.15	xxxx	−0.35	3.10	x	−0.48	3.70
1.50	xxxx	−0.25	2.95	xxxx	−0.27	2.95	x	−0.42	3.45
2.00	xxxx	−0.10	2.80	xxxx	−0.27	2.80	xxxx	−0.40	3.30
3.00	xxxx	−slow	2.65	xxxx	−0.26	2.65	xxxx	−0.39	3.10

* Degrees of flocculation indicated by number of x's, e.g., x = slight, xxxx = complete flocculation.

† Colloid concentration 1 gm. per liter. Residues equivalent to 1 gm. untreated colloid.

system. This indicates that the zeta potential had not been suppressed to the same degree by H_2SO_4 as by HCl.

The untreated Colts Neck colloid flocculated completely in the H_3PO_4 system at a concentration of 1.50 m.e. of acid per liter. At this concentration, the migration velocity of the particles was −0.29 μ. The removal of the basoid

constituents by deferration and by subsequent electrodialysis increased to 2.0 m.e. per liter the concentration of acid required for flocculation. At this concentration of acid, the mobility of the particles corresponded to $-0.27\ \mu$ for the untreated; $-0.32\ \mu$ for treatment A; and $-0.40\ \mu$ for treatment B. It is of

TABLE 5

Flocculation of Na-saturated Penn colloid by HCl, H_2SO_4, and H_3PO_4, and associated electrokinetic values

CONCENTRATION OF ACID	HCl			H_2SO_4			H_3PO_4		
	Flocculation*	Migration Velocity	pH	Flocculation*	Migration Velocity	pH	Flocculation*	Migration Velocity	pH
m.e./l.		*μ/sec./volt/cm.*			*μ/sec./volt/cm.*			*μ/sec./volt/cm.*	
				Untreated colloids†					
0.00	0	−0.88	6.30	0	−0.88	6.30	0	−0.88	6.30
0.50	xxxx	−0.26	3.60	xxxx	−0.38	3.75	0	−0.63	4.35
0.75	xxxx	−0.23	3.50	xxxx	−0.32	3.40	x	−0.50	4.00
1.00	xxxx	−0.15	3.30	xxxx	−0.29	3.35	xxx	−0.40	3.80
1.50	xxxx	−slow	3.05	xxxx	−0.22	3.05	xxxx	−0.35	3.50
2.00	xxxx	−slow	2.85	xxxx	−0.21	2.95	xxxx	−0.32	3 35
3.00	xxxx	0.00	2.75	xxxx	−0.20	2.75	xxxx	−0.27	3.20
				Residue "A"					
0.00	0	−0.84	6.05	0	−0.84	6.05	0	−0.84	6.05
0.50	xxxx	−0.48	3.50	xxx	−0.59	3.65	0	−0.80	4.25
0.75	xxxx	−0.34	3.30	xxxx	−0.47	3.35	0	−0.64	3.80
1.00	xxxx	−0.26	3.15	xxxx	−0.40	3.20	0	−0.47	3.60
1.50	xxxx	−0.20	2.90	xxxx	−0.37	3.05	xx	−0.42	3.40
2.00	xxxx	−0.17	2.65	xxxx	−0.27	2.90	xxxx	−0.40	3.25
3.00	xxxx	−0.16	2.60	xxxx	−0.26	2.70	xxxx	−0.34	3.10
				Residue "B"					
0.00	0	−0.95	6.40	0	−0.95	6.40	0	−0.95	6.40
0.50	xxxx	−0.61	3.50	xxx	−0.70	3.50	0	−0.82	4.30
0.75	xxxx	−0.44	3.35	xxxx	−0.55	3.35	0	−0.71	3.90
1.00	xxxx	−0.37	3.20	xxxx	−0.42	3.20	0	−0.56	3.70
1.50	xxxx	−0.33	3.00	xxxx	−0.40	3.00	0	−0.50	3.50
2.00	xxxx	−0.26	2.90	xxxx	−0.34	2.90	xxx	−0.45	3.35
3.00	xxxx	−0.16	2.70	xxxx	−0.31	2.70	xxxx	−0.41	3.10

* Degrees of flocculation indicated by number of x's, e.g., x = slight, xxxx = complete flocculation.

† Colloid concentration 1 gm. per liter. Residues equivalent to 1 gm. untreated colloid.

interest to note that the migration velocities of the particles in the H_3PO_4 system are generally higher and, like the H_2SO_4 system, are always more electronegative than in the HCl system. It was believed that the colloidal residues produced by treatment B would be rendered isoelectric by H_3PO_4 as a result of

the removal of basoids and the decreased adsorption of phosphate ions (7). The results in table 4, however, indicate that the colloidal particles in the H_3PO_4 system are never isoelectric, even at the highest concentration of acid used.

The electrokinetic and flocculation data from the study of the Penn colloid are presented in table 5. The mobility of the particles of this colloid during flocculation by HCl, H_2SO_4, and H_3PO_4 was similar to that of the Colts Neck colloid. The only exceptions are that the Penn colloid had a lower isoelectric pH than the Colts Neck, and the cataphoretic potential was reduced to a lesser degree at equivalent acid concentrations. The migration velocities of the flocculated Penn colloid particles were generally higher than those of the particles of Colts Neck colloid.

It will be recalled that in a previous contribution (8), in which the variations in ultimate pH values with deferration were discussed, it was said, ". . . the removal of the gel envelopes by the free iron oxide treatment activates some of the acidoid fractions and, as a consequence, an increased dissociation of H ions results." If this statement is correct, then the variations in ultimate pH should

TABLE 6

Relation between deferration of Colts Neck and Penn colloids and their ultimate and isolectric pH values

COLLOID	ULTIMATE pH (H_2O)			ULTIMATE pH (KCl)			ISOELECTRIC pH (HCl)		
	Un-treated	Residue "A"	Residue "B"	Un-treated	Residue "A"	Residue "B"	Un-treated	Residue "A"	Residue "B"
Colts Neck	4.5	4.3	4.1	4.20	4.20	4.00	3.55	2.55*	2.35*
Penn	4.6	4.45	4.1	4.25	4.30	4.00	2.75	1 85*	.

* Extrapolated.

be correlated with decreasing isoelectric pH values of the deferrated colloidal residues produced by treatments A and B.

Data in table 6 reconsider the ultimate pH values of the deferrated colloids in water and in *N* KCl in the light of these new data on the variations of the isoelectric pH values of the colloidal residues in HCl. A qualitative agreement seems to exist between the ultimate and the isoelectric pH values as shown, for example, by the Colts Neck colloid. By progressive deferration of this colloid, the ultimate pH values in water decreased from 4.5, for the untreated, to 4.3 with treatment A, and to 4.1 with treatment B. The corresponding isoelectric pH values of these samples were 3.55, 2.55, and 2.35. Similar decreases in isoelectric pH values of the Penn colloid by deferration are to be noted in table 6.

It is not clear why the colloidal residues, "A" and "B," should show increasing exchange acidity values, as reflected by the difference in ultimate pH values in water and in *N* KCl, without showing an increase in cation adsorptive capacity at pH 7.0. It is quite possible, however, that the newly activated acidoid bonds are operative only at low pH values and that the activity of acidoids decreases with increasing pH. This point will be investigated further.

SUMMARY

The removal of Fe and Al from soil colloids, by the free iron oxide method and by electrodialysis, produced colloidal residues the chemical and electrokinetic properties of which differed widely from those of the untreated colloids. It is not logical, therefore, to apply findings obtained by studying the deferrated colloid to the natural colloids.

The general conclusions from this study of the flocculation and electrokinetic behavior of deferrated Colts Neck and Penn colloids are as follows:

The concentration of HCl required for flocculation of deferrated Na-colloids was not markedly different from that required for flocculation of the untreated Na-colloids, but the cataphoretic charge associated with the deferrated colloids was generally higher than that of the untreated colloid.

The concentration of H_2SO_4 required for flocculation was approximately the same for the untreated colloid as for the deferrated residue "A," but the concentration required for flocculation increased with further deferration, as indicated by the behavior of residue "B."

The most marked effects from deferration were noted in the H_3PO_4 system, and particularly in the "B" residues of this series; the flocculating concentration of acid increasing from 1.5 to 2.0 m.e. per liter with the "B" residues of the Colts Neck colloid and from 1.0 to 2.0 m.e. with the "B" residues of the Penn colloid.

Deferration lowered the isoelectric pH of the colloids, and these lowerings were correlated with decreased ultimate pH values in water and in *N* KCl.

The differences in electrokinetic behavior and flocculation between the deferrated and the untreated colloids are explained on the basis of basoid removal during deferration and electrodialysis.

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A CALIBRATED SOIL PROBE FOR MEASURING FIELD SOIL MOISTURE[1]

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A need has long been felt for a simple device that could be used by the nontechnical worker for the determination of soil moisture condition. Newcomers to irrigated areas frequently find it difficult to judge the satisfactory timing of irrigations. The experienced irrigationist usually resorts to rule-of-thumb methods, and applies water when the crops definitely show signs of suffering, or when the irrigation best fits in with other cultural operations. Many such growers, aware of the shortcomings of this practice, have indicated a desire for some rational method by which they could determine irrigation schedules to the best advantage. Actual soil moisture measurement, in one form or another, has proved to be a means by which the grower can judge, very satisfactorily, the timing of irrigation. Crop or tree responses may give an indication, but some damage or lessening of yields, which usually cannot be regained, must occur before irrigation needs are made apparent. Rule-of-thumb or calendar methods are often hit or miss as far as maintaining maximum productivity is concerned.

A number of devices, some involving the measurement of electrical phenomena, have been devised, but as yet, have many limitations and cannot be considered as entirely fulfilling the requirements of a practical soil moisture indicator to be used by the average grower. The availameter[3] was developed as a practical device for soil moisture measurement by growers, but it has limitations as to type of soil and requires a certain amount of care on the part of the operator. The need for removing smooth, cohesive cores of soil with the soil tube is the most objectionable feature of the method. The principle on which it operates, namely, the measurement of soil plasticity or stability (resistance to deformation), has been shown to be correlated, on fairly uniform soils, with the corresponding soil moisture content.

The calibrated soil probe or soil stabilimeter, herein described, attempts to measure this same soil property on soil in place, without the necessity for removal of samples. As shown in figure 1, it consists of two units, the probe

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[3] Allyn, R. B., and Work, R. A. 1941 The availameter and its use in soil moisture control: I, II. *Soil Sci.* 51: 307–321, 391–406.

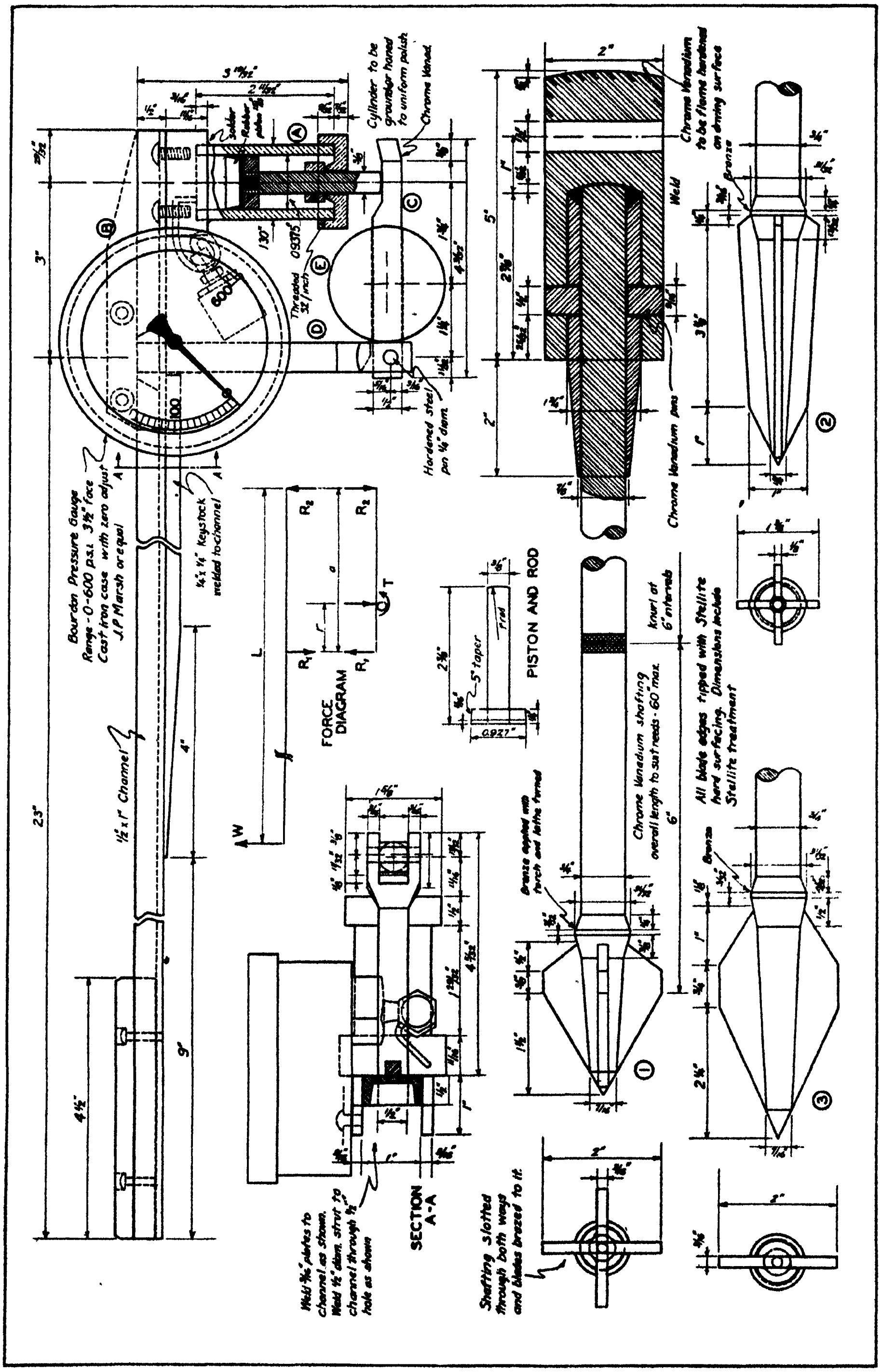

FIG. 1. CONSTRUCTION DETAILS OF THE STABILIMETER

and a calibrated, torque-measuring handle for measuring the soil resistance offered to the probe at various soil depths to which it is driven. The probe consists of three principal parts, the point, the shaft, and the driving head. The point consists of two diamond-shaped steel plates integrally fastened, at right angles to each other, to a $\frac{3}{4}$-inch diameter chrome vanadium steel shaft of suitable length. A convenient overall length has been found to be 52 inches, suitable for measuring moisture conditions to a depth of $3\frac{1}{2}$ feet. The driving head consists of two parts, a chrome vanadium sleeve shrunk over the end of the shaft and welded at the outer end, and the driving cap which slips over the sleeve. This cap is pin-connected to the sleeve with two $\frac{1}{2}$-inch hardened chrome vanadium steel pins, welded at their outer ends to the cap. The cap is heat-treated at the top to withstand the impact of the driving hammer. It has been found necessary to make the head in two parts as shown, in order to distribute excessive impact energy developed in driving. A 14-pound sledge hammer appears to cause less damage to the shaft than an 8-pound hammer.

Once the probe is driven to the desired depth, the stability determination consists of measuring the torque required just to overcome the resistance of the soil to rotation of the diamond-shaped probe point. This is accomplished by use of the calibrated handle. Essentially, the handle unit consists of a hydraulic cylinder (A) (fig. 1) which transmits the reaction, developed at a fixed distance from the axis of the probe, to a pressure gauge (B) which indicates the developed pressure and, by means of a conversion factor, the torque, since all other factors are held constant in the design. The hydraulic cylinder, of brass, finely ground and polished, utilizes a rubber piston cup of $\frac{15}{16}$-inch diameter and hydraulic brake fluid as the pressure transmission medium. The rubber piston cup is backed by a loose, floating, steel piston and rod which butts against the torque rod (C). This torque rod, which is pin-connected to strut (D), inserts loosely through a hole in the driving head (E), when the free end of rod (C) is swung out.

The analysis of the relation between torque in inch-pounds applied to the axis of the probe and the pressure gauge reading in pounds per square inch results in the equation $T = 2.19\ P$ and is developed from the force diagram of figure 1 in the following manner:

For equilibrium, a summation of the first moments of all forces about R_1 equals zero (clockwise moments assumed negative, and the handle considered as a free body, neglecting other forces). It follows then that

$$-W(L-a) + R_2a = 0; \text{ or } W \quad \frac{R_2a}{L-a} \ldots\ldots$$

The summation of horizontal forces normal to L is also zero and hence

$$-R_2 + R_1 - W = 0; \text{ or } R_1 = R_2 + W \ldots\ldots\ldots \quad 2$$

A summation of the first moments of all forces and torques acting on the torque rod about point 0 equals zero and

$$T - R_1r - R_2(a-r) = 0; \text{ or } T = R_1r + R_2(a-r) \ldots\ldots\ldots \quad 3$$

Combining 1 and 2 with 3 and simplifying,

$$T = R_2 a\left(1 + \frac{r}{L - a}\right) \quad \text{......} 4$$

P = pressure of fluid behind piston in pounds per square inch
A = internal cross-sectional area of cylinder in square inches = 0.690 (Diam. = $\frac{15}{16}$ inches)
a = 3 inches (from figure 1)
r = 1.25 inches (from figure 1)
L = 23.75 inches, effective length of handle (from figure 1)
$R_2 = P\,A = 0.690\,P$

Substituting these values in equation 4,

$$T = 2.19\,P \quad \text{......} 5$$

where T is the torque applied to the head of the probe in inch-pounds and P is the pressure-gauge reading in pounds per square inch.

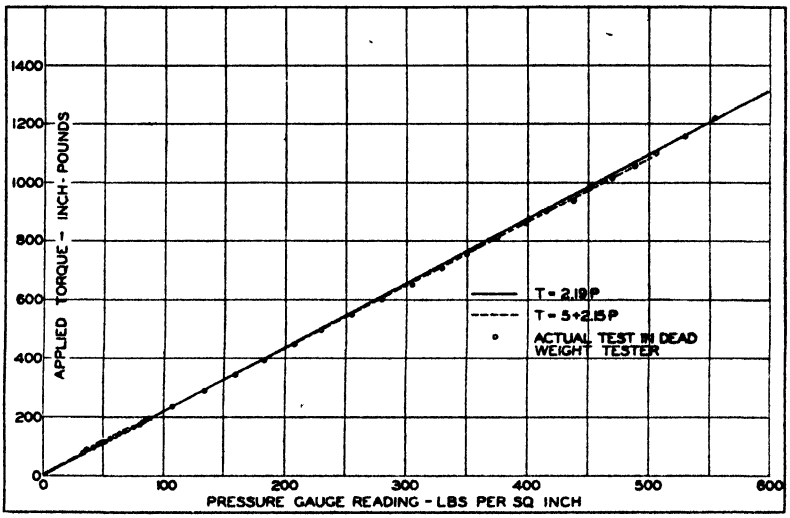

FIG. 2. PRESSURE-TORQUE RELATIONSHIP OF THE STABILIMETER

Figure 2 shows an actual calibration of the handle in a dead weight tester, compared with equation 5. The test results are indicated by the small circles. The conversion equation, $T = 5 + 2.15\,P$, resulting from actual test, was used in connection with the data of this investigation. The theoretical equation, $T = 2.19\,P$, would have been equally suitable, since the difference amounted to only 13 inch-pounds at a torque value of 1000 inch-pounds, or slightly over 1 per cent.

The dead weight tester consisted of a head and a short shaft similar to those of the probe in figure 1. The shaft, about 12 inches long, was inserted through two bearings rigidly fastened to a support. A scale beam-arm was then welded to the free end of the shaft and, by means of standard scale weights set at measured horizontal distances on this beam, any torque could be applied to the shaft, as the product of the weight by the horizontal beam distance from the axis

of the shaft. The initial value of moment due to the weight of the beam-arm, itself, was computed as the product of the weight of the beam by one-half the length of the beam. The calibrated handle was attached to the head in the same manner as shown in figure 1 and the pressure reading for any given scale beam setting taken as that which would just lift the scale beam from an outer support.

It will be noticed that the effective length of the handle (L) appears in equation 4 for the value of torque. This length is taken from a point at the center of the handle grip and is not a critical dimension. An examination of equation 4 will show that a variation of as much as 4 inches in the position of the hand will cause an error of about 1 per cent.

Three types of probe points are shown in figure 1. The cross-bladed point, No. 1, was used mainly in this investigation. It was found to be somewhat difficult however, to drive into heavy clay soils of low moisture content. Consequently, point 2 was designed for easier driving, yet to have approximately the same effective blade area as No. 1. Test results with point 2 were not so consistent or satisfactory as those with No. 1, particularly in drier soil. The reason for this is not entirely apparent. It is thought that, in driving, a cross-bladed point, such as No. 1 or 2, may cause some shattering of soil structure, mainly near the apex of the wedges of soil between the blades. Point 1, with the wider blades, extends farther into undisturbed soil, whereas the narrower blades of No. 2, when rotated, act on a greater proportion of shattered soil. The design of point 3 is presented as a possible solution to this difficulty. Although this blade has not, as yet, been field-tested, it is expected to have approximately the same resistance offered to its rotation as blade 1, and will be more easily driven, because of its single, one-piece blade. In cases where soil shattering in driving may have been troublesome with the original cross-bladed point, the single blade should cause less difficulty, since the soil is parted in only one straight cut.

In operation, the probe is driven to each of the various desired depths and the measuring handle is attached by insertion of the torque rod through the horizontal hole in the driving cap until strut (D) strikes the cap. Pressure is then slowly and uniformly applied to the handle and the pressure noted on the gauge at the point where the soil at the probe point gives way under the torque applied. The term "soil stability," as used in this paper, is defined as the torque in inch-pound units corresponding to the pressure read from the gauge at the instant that soil resistance is equalled. In practice, this is a definite and easily understood measurement and corresponds to the maximum pressure reading attained as a slow uniform rotation is given the probe by pulling on the handle. Abnormal soil conditions and obstructions, such as large stones or tree roots, are usually very evident by the high pressures developed. These high pressures immediately fall off as soon as the obstruction is loosened by the rotating point. Such readings, of course, should be discarded. Extensive work during one season has revealed very little difficulty from roots or small gravel.

The removal of the probe from the soil requires some form of lifting device.

A rapid-action jack,[4] recently developed, was found very satisfactory for this purpose. The jaw lifts directly under the shoulder of the head, and 15 to 20 seconds is usually sufficient to remove the probe from 3 or 3½ feet of soil.

The present investigation of the stabilimeter has been confined to heavy clay soils classified by the U. S. Bureau of Soils as Meyer clay adobe and having field capacities of 28 to 36 per cent. Since the same physical property of soil (its plasticity or stability) is involved, it is believed that the stabilimeter will operate satisfactorily on soils at least as light as those covered in the availameter investigation where soils with field capacities as low as 19 per cent were found to be accurately measured. It is possible that the stabilimeter will be successful on much lighter soils, because the soil is well restrained against the action of the blades. Thus confined, the lack of cohesiveness of the lighter soils probably would not be the critical factor as in the case of the availameter. Further investigation of this possibility would be desirable.

In figures 3, 4, and 5, the "mid-available range," designated as MR, refers to the moisture content half way between the field capacity and the wilting point or to the stability value half way between the stability values at the field capacity and at the wilting point. Figure 3 shows soil stability, or torque measurements with the stabilimeter, carried through an irrigation season on two adjacent orchard areas during 1940. Each soil moisture content and soil stability value shown is an average of approximately 10 determinations uniformly spaced over each plot area of slightly less than one acre. It is seen that the soil stability measurement varies in a regular way and in much the same manner as does the corresponding soil moisture content shown in the upper part of each section of the figure.

Figure 4 shows the correlation between the average soil stability values and the actual average moisture content at the various depths in these same orchards. The curves shown were not determined as the closest fit of the experimental points but are placed in accordance with a generalized relationship developed in figure 5. The fact that the curves do fit the points closely, substantiates the generalization to be shown. An examination of the accuracy of determination shown in figure 4 indicates that, generally, agreement much closer than 0.5 per cent was obtained. Only occasionally did the discrepancy reach a maximum of 1 per cent. In view of the fact that the moisture samples were taken with a tube at least 6 inches from the probe point, this correlation is considered very close. These data are illustrative of similar measurements made on approximately 30 other adjacent orchard plots of slightly varying field capacity but all with heavy clay soils.

In order to show the possibilities of development of a method for quickly constructing calibration curves for various soils in local areas from limited data, figure 5 is presented. In this figure, two groups of curves, A and B, are shown. These were constructed from actual soil stability and moisture content data obtained from all the orchard areas covered. Group A curves are

[4] Allyn, R. B. 1940 A rapid-action soil tube jack. *Soil Sci.* 50: 49–51.

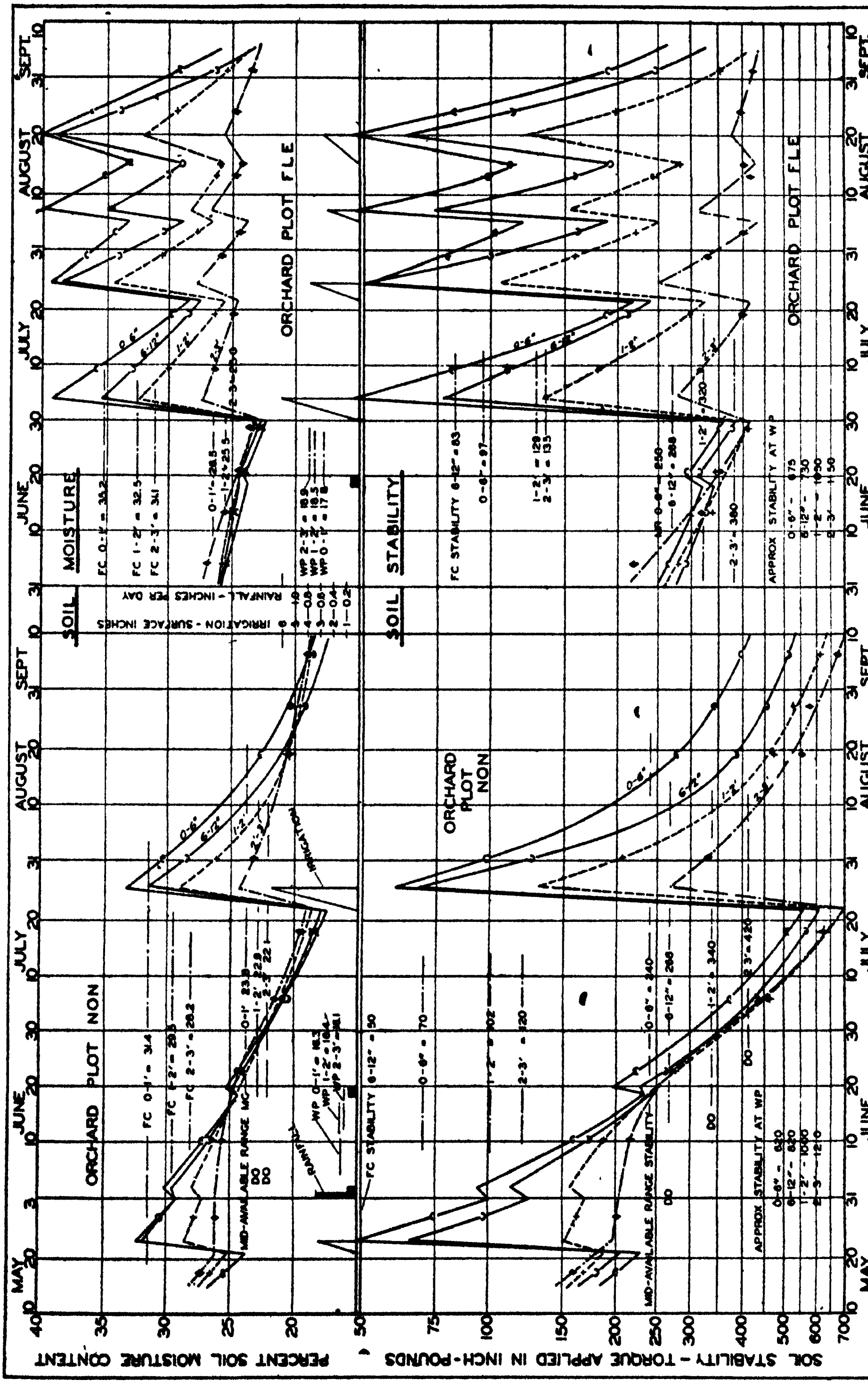

Fig. 3. Comparison of Soil Moisture and Soil Stability Measurements in 2 Orchards during 1940 Season
Lines are extrapolated from the nearest observed point to the time of beginning or ending an irrigation

correlation or calibration curves between soil stability and soil moisture content for soils having various field capacity values, which at the 0- to 6-inch depth, range from 31 to 36 per cent. The range of field capacity values is limited, of course, because all the soils included in this investigation were of the heavier types. In all cases, the field capacity values, as determined, decreased 3 to 4 per cent from the top foot to the 3-foot depth, and for that reason the field capacity values at the third foot depth are limited between 28 and 32 per cent.

In using these curves for determining a stabilimeter calibration it is only necessary to determine or approximate a value for the field capacity at the various soil depths.

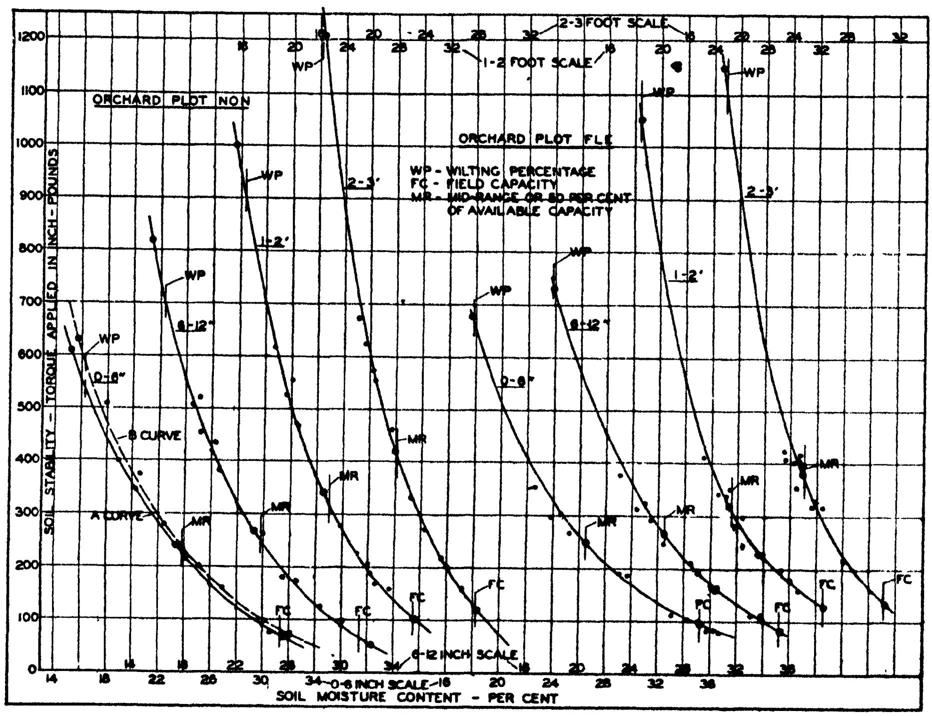

FIG. 4. SOIL STABILITY VERSUS SOIL MOISTURE CORRELATION CURVES AT SEVERAL DEPTHS IN TWO ORCHARDS

A closely approximate curve for each soil depth may then be interpolated from the group by paralleling the two adjacent curves for the soil depth in question. An alternative method would consist of making actual soil stability measurements in the field at several locations and plotting their average value, at each depth, against the corresponding average soil moisture content, as determined by sampling and oven-drying, on the proper chart of figure 5. The position of this point on the chart will help to determine the most likely curve to be selected. In this investigation, data were obtained at four depths: 0–6 and 6–12 inches and 1–2 and 2–3 feet. In practical and routine irrigation management, these curves might best be combined into only one or

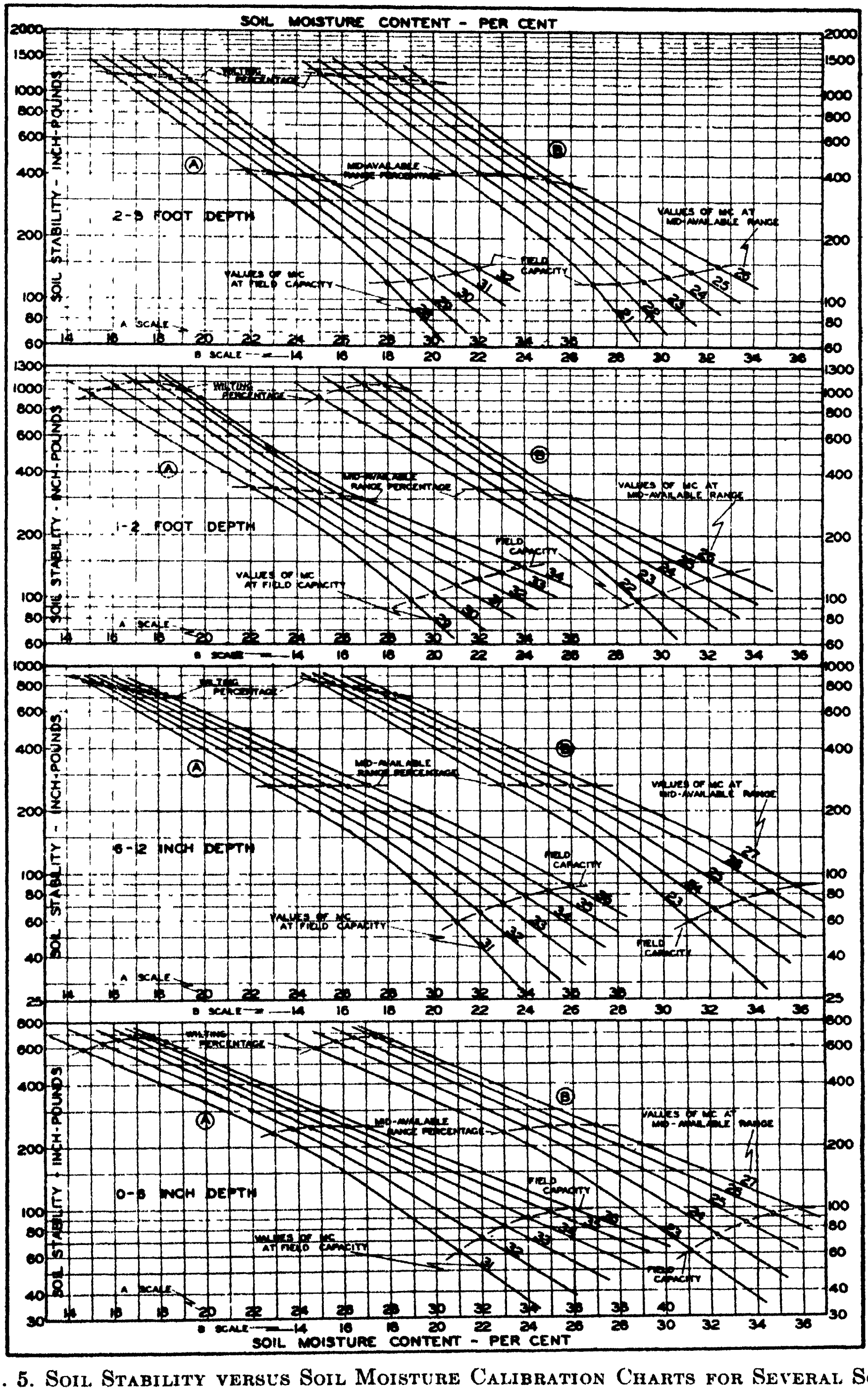

Fig. 5. Soil Stability versus Soil Moisture Calibration Charts for Several Soil Depths

Lines are extrapolated from the nearest observed point to the time of beginning or ending an irrigation.

two depth separations, for simplicity, and all field measurements within each depth zone, averaged.

The accuracy of these approximate calibration curves when a definite field capacity value is known is apparent from the fit of the curves with the data of figure 4 where soils near both extremes of the range investigated are shown. This close agreement was also true in the great majority of all the orchard plots investigated.

The group B curves of figure 5 are similar to those of group A except that the B grouping is according to the moisture content value midway between field capacity and the wilting percentage. In those few cases where an A group curve did not closely fit the actual field data, a curve approximated from group B, requiring knowledge of the wilting percentage as well as the field capacity for the soil in question, resulted in a closer agreement. An example of this will be noted in the 0–6-inch curve of plot NON, shown in figure 4. Group B curves were usually as good as or better than group A curves in all the test areas. Thus, where both the wilting point and field capacity constants are known for the area in question, a somewhat truer curve, in some cases, may be expected by using the group B charts. Preferably, they should be used also where a definite wilting value is known, and the field capacity, only approximately. Since group A curves, however, were found to be as good in a great proportion of the tests, their general use would be more convenient, since only the field capacity value is required. In the alternate method of making one or two initial, average, stability-moisture content determinations in the selected area, either group should yield the same curve.

The stability values to be expected at the extremities of the available range are indicated by the intersecting dashed lines, i.e., the wilting percentage and field capacity stability values on the charts of both groups in figure 5. These intersections were obtained by extensive field and laboratory determination of these moisture constants for the field plots used in this investigation.

The stability values at the extremities of the available moisture range as determined from the charts of figure 5 are shown for each soil depth of the orchard areas in figure 4. For instance, the 1–2-foot depth of plot FLE, figure 4, with a determined field capacity of 32.5 per cent, defines a curve parallel to, and midway between, the 32 and 33 per cent group A curves for the 1–2-foot depth of figure 5. This curve intersects the dashed lines of field capacity and wilting percentage at stability, or torque values, of 129 and 1050 inch-pounds, respectively. These values appear on the 1–2-foot curve of plot FLE in figure 4 as the large, black circles at the extremities of the curve. The vertical lines intersecting the curve, marked FC and WP, indicate the exact moisture content at the field capacity and wilting percentage, as determined by field and laboratory methods. In this particular case, there is exact agreement between the actual determination and the approximate values from figure 5.

The intersecting dashed lines of figure 5, indicating the mid-available range point, were determined from the moisture content value midway between the field capacity and the wilting percentage, and correspond to the moisture

content at 50 per cent of the available capacity for each of the curves shown, whether group A or B. In the illustration given above, the 32.5 per cent curve intersects the mid-range or MR line at 320 inch-pounds, and this point is shown as a large, black circle in the 1–2-foot curve for plot FLE of figure 4. The vertical line, MR, indicates the moisture content actually determined to represent the moisture condition midway between field capacity and wilting percentage. Here again, exceedingly close agreement is evident. The remaining curves of figure 4 also show agreement, usually much closer than 1 per cent, with respect to these three available moisture range points.

It will be apparent that a stabilimeter calibration curve can be determined from very limited local data which will closely define the limits of available soil moisture. Such a calibration curve can be easily converted into terms of available moisture with the wilting percentage value as the point of zero availability, and the field capacity representing 100 per cent. A dial might be applied to the instrument, calibrated in this manner, so that available moisture would be read directly from the pressure gauge. From figure 5, it is apparent that in the range of soils shown, the wilting percentage stability value is substantially constant, being about 650 inch-pounds for the 0–6-inch depth, 780 for the 6–12-inch depth, 1000 for the 1–2-foot depth, and 1200 for the 2–3-foot depth. The deviations from these averages are relatively unimportant in terms of actual moisture content. Although there is a somewhat greater percentage difference among stability values at the field capacity point, this apparent constancy of the wilting percentage stability value would indicate the usefulness of stabilimeter measurements, directly, as a guide to irrigation practice, without recourse to actual calibration in moisture content units. This conclusion is further substantiated by the fact that at the mid-range of available moisture the soils investigated show the following average stability values according to the charts of figure 5. These are: 0–6-inch depth—245 inch-pounds; 6–12-inch—265; 1–2-foot—325; and the 2–3-foot—395 inch-pounds. An investigation of the error involved in the assumption of these constant values for the soils covered in this study will show a discrepancy of less than 0.5 per cent of soil moisture.

In figure 3, where actual soil moisture and soil stability measurements are shown for two separate orchard plots during an irrigation season, the values of soil moisture and soil stability at the field capacity, the mid-available range, or MR point, and the wilting percentage are shown, where the scale permits, as horizontal lines. The FC, MR, and WP values were taken from the respective points in the charts of figure 5. An examination of the dates on which soil moisture was withdrawn to the mid-available range point will indicate close agreement between the two types of moisture measurement. The poor moisture penetration into the 2–3-foot depth is very evident in the stability measurement.

Since one method of using the charts of figure 5 involves the knowledge of the field capacity value of soils and since its determination, apparently, has no widely accepted or standardized technique of determination, it may be important to set forth the method used in connection with the soils of this inves-

tigation. Work and Lewis[5] have described a method which consists, essentially, in averaging the three highest plot average moisture content values determined by soil sampling at times when the soil was considered to be holding all the capillary water possible, and after any excess water had drained away. In orchard practice, in this locality, this consisted of sampling at twice-monthly intervals in the period from just prior to bloom, following winter rains, until the first irrigation. Thereafter, samples were taken following each irrigation as soon as it was possible to work on the plots. Because of exceptionally sticky mud conditions, this was usually from three to four days after the irrigation was completed.

The method used in connection with the present investigation is very similar. In each of the 30 plot areas, detailed sampling has been undertaken for 6 or more years. The 18 highest plot mean values occurring during the 6-year interval were averaged at each depth, and this value was taken as the field capacity. This procedure, although purely arbitrary, has proved quite satisfactory in practice.

In the work with the stabilimeter, the first foot soil depth was separated into two equal horizons, the 0–6-inch and the 6–12-inch intervals, in order to investigate the usefulness of the stabilimeter at the shallow depths. Since previous field capacity determinations were made, however, on the entire foot as a unit, the two 6-inch portions, necessarily, were assumed to have equal field capacities and all data in this paper follow this assumption. It is probable that the topmost 6-inch layer has a somewhat higher value than the lower, since field capacity in these soils decreases with increase in depth, partly perhaps, because of moisture penetration difficulties. Thus, if the proper field capacity values had been determined for each 6-inch layer in the top foot, the inconsistency of higher stability in the 0–6-inch than in the 6–12-inch depth, at field capacity, would perhaps have been eliminated. This is a minor consideration, however, and for practical orchard irrigation these depths can be advantageously combined.

SUMMARY

A new device, known as the stabilimeter, for quick field determination of soil moisture conditions is described. The apparatus consists, essentially, of a diamond-shaped blade point mounted on a shaft, by means of which the blade point can be driven to the desired soil depths. The measurement of the resistance of the soil to rotation of this point is termed "the soil stability" and is evaluated in terms of torque in inch-pound units by the use of an especially designed handle which may be attached quickly to the head of the shaft.

This stability measurement, when correlated with the corresponding soil moisture content, shows a consistent relation by means of which soil moisture content may be estimated, usually within 0.5 per cent, in heavy soils such as

[5] Work, R. A., and Lewis, M. R. 1934 Moisture equivalent, field capacity, and permanent wilting percentage and their ratios in heavy soils. *Agr. Engin.* 15: 355–362.

were covered in this investigation. Use of stability measurements as a direct measure of soil moisture conditions is shown, and a generalized relationship is developed to facilitate the preparation of a soil moisture-stability calibration for an area without the necessity of detailed laboratory work.

The range of soil types on which this method would satisfactorily operate was not determined, since the investigation was confined to heavy soils. It is believed, however, that satisfactory operation will be found on soils as light as clay loams and, quite possibly, on much lighter soils.

ADSORPTION AND FIXATION OF COPPER IN SOME SANDY SOILS OF CENTRAL FLORIDA

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Copper has been used for many years in Florida citrus culture to correct a condition popularly called "ammoniation" or "dieback" and recently classified as "copper deficiency" (2). Direct soil application has usually been satisfactory, though it is generally more expedient to use copper in a nutritional spray. Very little is known about the fate of copper added to the sandy soils of central Florida. With a single salt extraction, Peech (4) recovered only a small fraction of a rather high application of copper sulfate to acid Norfolk fine sand. Still, copper-deficient citrus trees on Norfolk soils respond fairly well to soil additions of copper. It seems that the quantity of easily replaceable copper as a reliable criterion of its supply to citrus may be questioned. Although the copper applied may be fixed, the amount offered to the trees from many slowly soluble or difficultly replaceable forms may be adequate.

Sieling (5) has described a simple and rapid method whereby the adsorption of copper is used to determine the exchange capacity of soils. Even though copper may be fixed by many Florida soils, it was thought the fixation capacity might be so small in comparison with the exchange capacity that this method would be of value to soil workers in Florida. In this work Sieling's method was tested for several Florida soils, and an effort was made to learn something of the relationship between adsorption and concentration of copper in solution. In addition, a study of fixation of copper by several soils was made and is included in this report. An effort was made to distinguish between ordinary exchange adsorption and fixation by roughly measuring the recovery of copper from several soils and soil materials with salt and acid extractants.

EXCHANGE CAPACITY AND COPPER ADSORPTION

The soils used were taken from the stock of samples collected by Peech (3) in a survey of citrus soils, on which he reported rather complete chemical studies. Some of his data are used here for comparative purposes.

To determine the exchange capacity of a soil, Sieling added a copper-acetate–acetic-acid solution (0.2 N Cu^{++} and pH 4.6) to a weighed soil sample in distilled water until the symmetry concentration was about 1.5. After the soil-solution mixture was shaken and a portion filtered, a suitable aliquot was taken. The copper in solution was converted to the ammonium complex, and the reduction in concentration due to adsorption was estimated by comparison with a set of copper color standards. From the amount of copper adsorbed and the weight of soil used, the exchange capacity was calculated. The same method, slightly modified, was used in this study. Instead of using a set of copper color stand-

ards, the concentration of the ammoniacal copper was estimated from readings made with a photoelectric colorimeter. A standard curve was plotted from readings made on colored standards diluted from a 0.2 *N* $Cu(NO_3)_2$ solution prepared from weighed electrolytic copper. Concentrations corresponding to readings made on unknowns could be read from the standard curve.

TABLE 1

Comparison of copper acetate and ammonium acetate methods for determining exchange capacity of soils

SAMPLE NUMBER	SOIL TYPE	SOIL pH	$NH_4C_2H_3O_2$ EXCHANGE CAPACITY	$Cu(C_2H_3O_2)_2$ EXCHANGE CAPACITY	PERCENTAGE* SATURATION WITH COPPER
			m.e./100 gm.	*m.e./100 gm.*	
290	Norfolk sand	6.06	1.39	0.80	57.6
292	Norfolk sand	6.25	1.41	1.20	85.2
294	Norfolk sand	5.21	1.51	0 60	39 7
124	Norfolk fine sand	6 30	1.71	1.48	86 6
120	Norfolk fine sand	4.80	1.86	1.00	53.6
218	Norfolk fine sand	4.94	2.50	1.48	59.2
186	Norfolk fine sand, hammock phase	5.66	4.35	2.00	46.0
310	Blanton fine sand	6.19	3 51	2.51	71.4
214	Orlando fine sand	5.16	6.62	2.70	40.4
224	Gainesville fine sand	5 49	7.10	3.30	46.4
274	Portsmouth fine sand, hardpan phase	4 55	2.95	2.40	81 4
276	Portsmouth fine sand	5.94	3.70	3 50	94 4
156	Portsmouth fine sand	5.14	9.35	4.20	45 0
282	Eustis fine sand, dark-colored phase	5.69	6.46	3.60	55.8
162	Eustis fine sand	5.64	2.84	1.60	56.4
270	Parkwood fine sand	5.24	3.62	2.75	76.0
259	Parkwood fine sand	6.26	4 58	3.30	72.0
148	Parkwood fine sand	6.20	5.75	3.60	62.6
157	Parkwood clay loam	8.31	6.60	7.60	115.2
147	Parkwood clay loam	8.26	7.68	5 20	67.7
230	Parkwood fine sandy loam	6.94	14.7	5 60	38.0
269	Bladen fine sandy loam—subsoil	5.86	21.6	5.50	25.4

* Ammonium acetate exchange capacity taken as 100 per cent.

In table 1, the results are shown for several soils in comparison with those obtained by the ammonium acetate method. The copper method gave consistently lower values, although a concentration greater than twice the soil exchange capacity as determined by the ammonium acetate method was used in all cases. Assuming the ammonium values as reliable bases for calculation, the percentage saturation with copper for each soil was computed and is also shown.

The lowest percentages are for the soils having the highest capacity for ammonium adsorption. Hence, the discrepancies cannot be attributed to the use of soils of low exchange capacities.

Since many of the soils had adsorbed copper in amounts equivalent to only a small fraction of their predetermined exchange capacities, the question arose as to what relationship might exist between adsorption and concentration of copper in solution when the pH and the soil dilution are held constant. A series of copper acetate solutions were prepared, varying in concentrations from 0.1 to 0.5 N. Each of these was adjusted, by means of a glass electrode pH meter, to pH 4.6 with acetic acid. They were standardized by comparing the photoelectric colorimeter readings made on suitable dilutions with the standard curve. A 10-gm. sample of soil was added to each of several 25-ml. portions of the copper solution series. The suspensions were shaken frequently for several hours and allowed to stand overnight. The supernatant liquid of each suspension was filtered through a Whatman No. 30 paper. As a check on copper adsorption by the filter paper, the original solution was also filtered and treated subsequently in the same manner as the copper-soil filtrate. Suitable aliquots were taken and made to volume in ammonium hydroxide in volumetric flasks. In each case, the copper concentration was determined, the copper adsorbed calculated, and the pH of a portion of each filtrate determined.

In figure 1 are shown the relationships found between equilibrium copper concentration and copper adsorption and also equilibrium solution pH for four soils. At the comparatively very high concentration of 0.25 N, the Orlando soil is apparently saturated with copper. This is at an adsorption value close to the exchange capacity. The other three soils adsorbed copper continuously as the concentration increased. Although there is a flex in each of the curves for the Norfolk soils above the exchange capacity level, there is no certain connection between this flex and the exchange capacity. A copper saturation value for the Gainesville soil is not shown with any concentration below a nearly saturated solution of $Cu(C_2H_3O_2)_2$.

The initial pH value plotted in each curve is 4.6, that of the original copper solutions. With a very dilute copper solution added to the soil, the resulting pH would tend toward that found for the soil in a 1:1 soil-water dilution. This tendency is shown with the second point on the Gainesville-pH solution curve. With three of the soils, the exchangeable acidity is apparently about equally displaced with copper above 0.03 N. A very low concentration seems effective with the virgin Norfolk soil. With increasing concentration, the pH continuously approaches that of the original solutions. The combined effects of dissociation of H^+, displacement of H^+, and salt buffering cannot be accurately mapped in the dilute range, but it is evident that with these soils of comparatively low exchange capacities, the buffering of 0.05 to 0.2 N $Cu(C_2H_3O_2)_2$ at pH 4.6 with acetic acid is not realized. With a large number of soils, considerable variation in pH may be expected in the equilibrium copper solutions. The result would depend not only on the copper-ion concentration but also on the nature of the soil, its exchangeable acidity, and other adsorbed cations.

Sieling (5) also found that copper adsorption increased with the concentration, but he showed no results for the test above a concentration greater than twice the soil exchange capacity, where he found about 100 per cent saturation for two

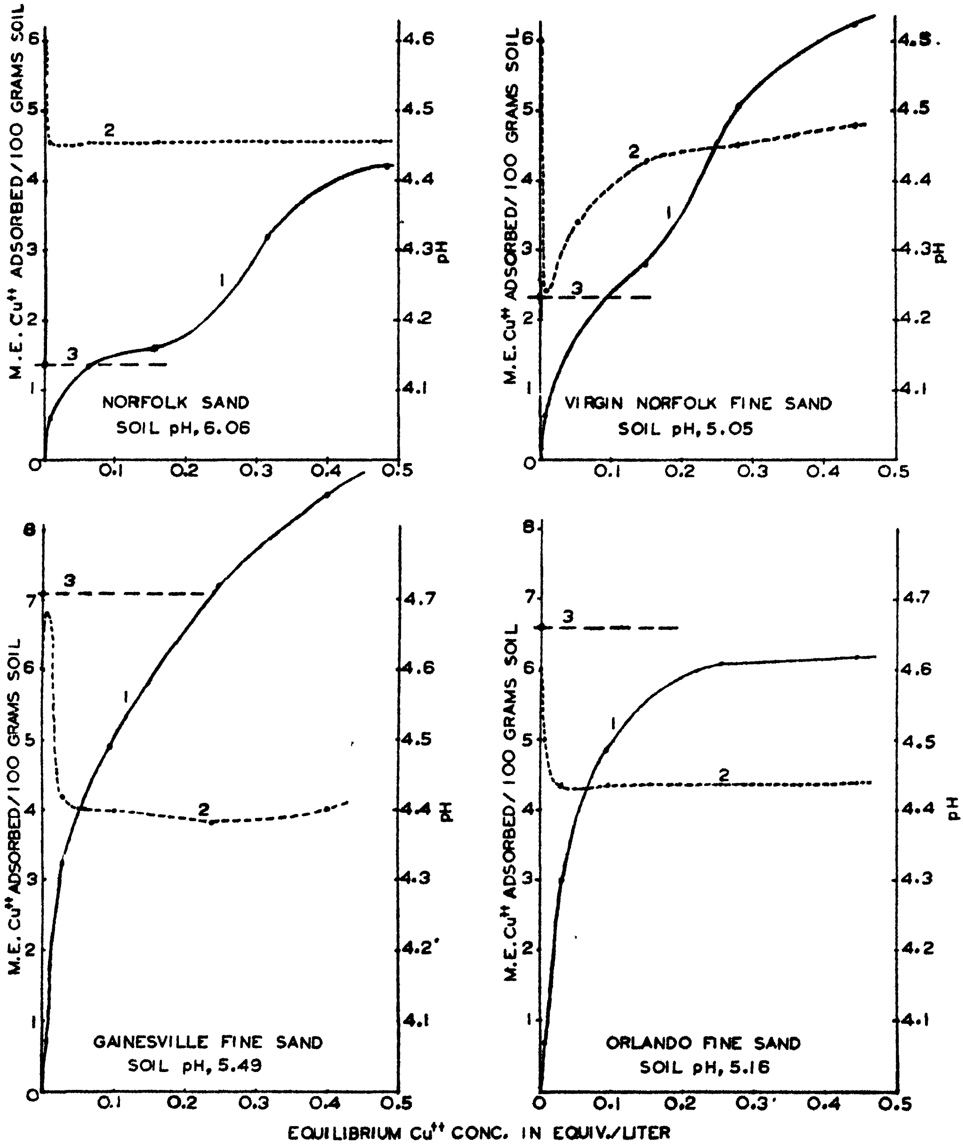

FIG. 1. COMPARISON OF THE RELATIONSHIPS BETWEEN ADSORPTION AND EQUILIBRIUM SOLUTION CONCENTRATION OF CUPRIC ION AND ALSO EQUILIBRIUM SOLUTION pH FOR FOUR FLORIDA SANDY SOILS

Curve 1, copper adsorption-concentration relationship; curve 2, equilibrium pH cupric-ion concentration relationship; and curve 3, ammonium acetate exchange capacity level for the soil.

soils but only 80.3 per cent for a bentonite clay sample. Perhaps many of the soils he used would also remove from solution greater amounts of copper than expected from the exchange capacity as determined by adsorption of NH_4^+. At least, this point should be carefully tested for mineral soils before the method is used.

The exchange properties of soils are doubtless related to the adsorption of copper. Bower and Truog (1) found for weak bases that cations of valences greater than unity gave greater exchange adsorption values than monovalent cations with the same soil. When methyl alcohol was used instead of water as the solution medium, the values obtained by using monovalent and polyvalent cations were more nearly in agreement. They concluded that the adsorption of hydrolysis products like $Mg(OH)^+$ would account for the high values. Thus, there is the possibility that much copper can be adsorbed as $Cu(OH)^+$, even at pH 4.6.

RECOVERY OF COPPER FROM COPPER-TREATED SOILS

Six soils types represented by samples taken from our soil survey stock were used for this study. Three duplicate sets of 50 gm. of each were placed on Whatman No. 30 filter paper in funnels and leached with 200 ml. 0.2 *N* $Cu(C_2H_3O_2)_2$ adjusted to pH 4.6 with acetic acid. Each sample was then leached with 150 ml. of 80 per cent alcohol. Samples of one set were each leached with 200 ml. *N* HCl. Samples of the second set were leached with five successive 100-ml. volumes of 1.7 *N* NaCl adjusted to pH 4.6 with acetic acid, and then with 100 ml. *N* HCl. The organic matter was destroyed in the salt leachates by heating gently with 2 ml. 30 per cent H_2O_2. The acid leachates were evaporated to near dryness, 5 ml. conc. HNO_3 and 2 ml. conc. HCl were added, and the leachates were again evaporated, this time to dryness. They were then taken up in a suitable quantity of dilute HCl. The salt solution extracts were evaporated to suitably smaller volumes. Each sample was added to a volumetric flask and heated with ammonia to flocculate sesquioxides present and then after cooling made to volume, mixed, stoppered, and allowed to stand overnight. Colorimetric readings were made on aliquots drawn off with a pipette.

The amount of copper replaced by each leaching is shown in table 2. The values shown are averages of duplicates, which were generally in good agreement. The quantity of copper removed with 100 ml. *N* HCl is less than the sum removed in the NaCl-HCl or $BaCl_2$-HCl sets in every case. Small quantities of copper were removed with further leaching with *N* HCl. Sets II and III yielded amounts somewhat higher than can be accounted for by the exchange capacities. It is clear that much of the copper is held in slowly soluble nonreplaceable or slowly replaceable forms. The amount of copper removed by the water leaching is a rough measure of the combined effects of solution and hydrolysis. Since copper-saturated soil samples were used, this value does not have much practical significance.

The greater effectiveness of NaCl over $BaCl_2$ is surprising, since Ba^{++} is generally known to be a much more effective replacing cation than Na^+. Pos-

sibly much of the copper came through the filter paper in union with very finely dispersed humates. Ba^{++} was probably more effective in keeping the colloids flocculated and subject to strict replacing action.

It was thought that the time of contact or the drying of the soil might have had some effect on the fixation of copper. This next experiment was designed to check on these factors as well as to learn more about the effects of cation

TABLE 2

Copper displaced from six copper-saturated soil types by three different leaching procedures

Values expressed in milliequivalents leached per 100 gm. of soil

	SOIL TYPE					
	Norfolk fine sand (virgin)	Norfolk very fine sand	Norfolk fine sand	Blanton fine sand	Eustis fine sand	Gainesville fine sand
Soil pH	5.00	5.29	4.90	5.49	6.29	6 09
$NH_4C_2H_3O_2$ Exchange Capacity	2.35	6.25	5.00	4.70	5.27	6.65
Set I—*N* HCl:						
1st 100 ml. leached with HCl	2.20	4.50	4.20	4.70	6.86	7.25
2nd 100 ml. leached with HCl	0.05	0.12	0.11	0.10	0.07	0.07
Set II—1.7 *N* NaCl adjusted to pH 4.6 with $HC_2H_3O_2$:						
1st 100 ml. leached with NaCl	1.60	3.38	3.28	3.38	4.55	4 82
2nd 100 ml. leached with NaCl	0.35	1.04	0 66	0.64	1 24	1.46
3rd 100 ml. leached with NaCl	0.13	0.34	0.21	0.23	0.33	0 39
4th 100 ml. leached with NaCl	0.12	0.21	0 13	0.15	0.29	0.28
5th 100 ml. leached with NaCl	0 06	0.15	0.11	0.11	0.20	0.21
Total	2 26	5.12	4 39	4.51	6 61	7.16
Final leaching with *N* HCl	0.55	1.19	0.92	1.02	1.78	1.46
Set III—1.7 *N* $BaCl_2$ adjusted to pH 4.6 with $HC_2H_3O_2$:						
Water-soluble Cu^{++}, leached with 100 ml. distilled water	0.24	0.25	0.21	0.14	0.28	0.34
1st 100 ml. leached with $BaCl_2$	0.93	1.70	1.71	1.66	3.87	3.25
2nd 100 ml. leached with $BaCl_2$	0.43	0.55	0.47	0.92	1.10	1.45
3rd 100 ml. leached with $BaCl_2$	0.21	0.41	0.37	0.44	0.58	0.69
4th 100 ml. leached with $BaCl_2$	0.10	0.23	0.19	0.23	0.28	0.34
5th 100 ml. leached with $BaCl_2$	0.11	0.28	0.21	0.22	0.28	0.32
Total	2.02	3.42	3.16	3.61	6.39	6.39
Final leaching with *N* HCl	0.54	1.46	1.28	1.18	0.98	1.22

concentration and acidity. The Eustis soil used previously (table 2) was chosen. Nine 50-gm. samples were saturated, as before, with a $Cu(C_2H_3O_2)_2$ solution (pH 4.68). One sample was leached immediately with two successive 100-ml. volumes of 1.7 *N* NaCl (pH 4.68), then with nine successive 100-ml. volumes of *N* $NaC_2H_3O_2$ (pH 4.68), and finally with 100 ml. *N* HCl. Four samples were treated similarly except that two were kept moist while two others were allowed to air-dry before leaching.

The results are shown graphically in figure 2. The values for the air-dried and moist samples are the averages of closely agreeing duplicates. Although time may have some slight effect on fixation, the effect of drying is not significant. It is especially noticeable that $NaC_2H_3O_2$ is more effective in removing copper than NaCl even at a lower equivalent concentration. Appreciable quantities of copper were found after a liter of salt had leached through the samples. From the previous experiment, it is doubtful that the twelfth leaching with HCl completely exhausted the fixed copper.

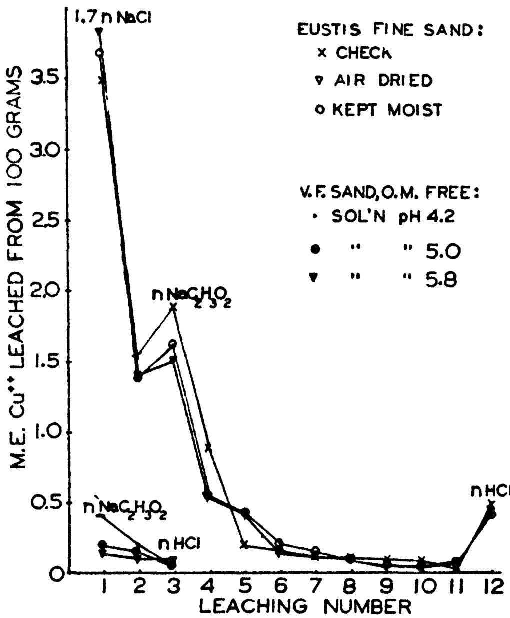

FIG. 2. EFFECT OF AIR-DRYING ON THE REMOVAL OF COPPER FROM COPPER-SATURATED EUSTIS FINE SAND BY TWO SUCCESSIVE 100-ML. LEACHINGS WITH NaCl, THEN NINE WITH $NaC_2H_3O_2$, AND FINALLY ONE WITH *N* HCl. THE REMOVAL OF COPPER FROM COPPER-SATURATED ORGANIC-MATTER-FREE VERY FINE SAND IS ALSO SHOWN

The salt solutions were adjusted to pH 4 68 with acetic acid

The treatments on the remaining four (air-dried) samples are shown in table 3 together with the pH of the leachates and the amounts of copper removed. The results for the first 300 ml. are similar to those shown in figure 2. When dilute $NaC_2H_3O_2$ or $HC_2H_3O_2$ was used, the copper removed decreased. Even *N* $HC_2H_3O_2$ is apparently no more effective than *N* $NaC_2H_3O_2$. When *N* $NaC_2H_3O_2$ followed $HC_2H_3O_2$, however, there was always a marked removal of copper. The replacement of H^+ from the soil by Na^+ probably had an effect which the pH value of the accumulated leaching solution fails to show clearly. The acidity of 100 ml. of leachate might have been quite different from that of a small portion of the same leachate as it passed from the soil.

It took more than one day to complete the leaching, and the effect of time is

TABLE 3

Removal of copper from copper-saturated Eustis fine sand by leaching

Successive 100-ml. volumes of leaching solutions—1 7 *N* NaCl, *N* $NaC_2H_3O_2$, and 0.1 *N* $NaC_2H_3O_2$ adjusted to pH 4.68 with $HC_2H_3O_2$

LEACHING NUMBER	SAMPLE 2			SAMPLE 3			SAMPLE 6			SAMPLE 9		
	Leaching solution	pH of leachate	Cu^{++} removed	Leaching solution	pH of leachate	Cu^{++} removed	Leaching solution	pH of leachate	Cu^{++} removed	Leaching solution	pH of leachate	Cu^{++} removed
			m. e./ 100 gm.			*m. e./ 100 gm.*			*m. e./ 100 gm.*			*m. e./ 100 gm.*
1	1.7 *N* NaCl	4.74	3.60	1.7 *N* NaCl	4.77	3.95	1 7 *N* NaCl	4.73	3 50	1.7 *N* NaCl	4.78	3 85
2	1.7 *N* NaCl	4.68	1.45	1 7 *N* NaCl	4.68	1.40	1 7 *N* NaCl	4 68	1.55	1 7 *N* NaCl	4.68	1.50
3	*N* $NaC_2H_3O_2$	4.63	1.65	*N* $NaC_2H_3O_2$	4.60	1.50	*N* $NaC_2H_3O_2$	4 62	1.85	*N* $NaC_2H_3O_2$	4.62	1.65
4	0.1 *N* $HC_2H_3O_2$	4.52	0.22	*N* $NaC_2H_3O_2$	4.68	0.56	*N* $NaC_2H_3O_2$	4.70	0 56	*N* $NaC_2H_3O_2$	4.68	0 60
5	0.1 *N* $HC_2H_3O_2$	4.05	0.10	*N* $NaC_2H_3O_2$	4 70	0.42	*N* $NaC_2H_3O_2$	4.70	0 34	0 1 *N* $HC_2H_3O_2$	4.45	0.12
6	*N* $NaC_2H_3O_2$	4.63	0.80	*N* $NaC_2H_3O_2$	4 68	0.18	*N* $NaC_2H_3O_2$	4 68	0.18	0.1 *N* $HC_2H_3O_2$	3.85	0.10
7	*N* $NaC_2H_3O_2$	4.68	0.27	0.1 *N* $HC_2H_3O_2$	4.50	0.05	*N* $HC_2H_3O_2$	3.82	0.15	0.1 *N* $HC_2H_3O_2$	3.83	0 09
8	*N* $NaC_2H_3O_2$	4.68	0.17	0 1 *N* $HC_2H_3O_2$	3.82	0 04	*N* $HC_2H_3O_2$	3.23	0 04	0.1 *N* $HC_2H_3O_2$	3.86	0.02
9	*N* $NaC_2H_3O_2$	4.68	0 015	0.1 *N* $HC_2H_3O_2$	3.70	0.01	*N* $NaC_2H_3O_2$	4.54	0.06	0.1 *N* $NaC_2H_3O_2$	4.47	0.02
10	0.1 *N* $NaC_2H_3O_2$*	4.58	0.045	0.1 *N* $HC_2H_3O_2$*	3 82	0.015	*N* $NaC_2H_3O_2$	4 67	0 055	0.1 *N* $NaC_2H_3O_2$*	4.58	0.03
11	0.1 *N* $HC_2H_3O_2$	4.48	0 025	*N* $HC_2H_3O_2$	3.15	0.05	*N* $NaC_2H_3O_2$*	4.68	0 13	0.1 *N* $NaC_2H_3O_2$	4 58	0.025
12	*N* $NaC_2H_3O_2$	4.53	0.14	*N* $NaC_2H_3O_2$	4 53	0.12	*N* HCl		0.52	*N* HCl		0.84
13	*N* HCl	.	0.42	*N* HCl		0 18				.	.	...

* Stood overnight wet with previous leaching solution.

clearly shown by an increase in every case with the first leaching after standing overnight.

The fixation of copper by finely ground sand is also shown in figure 2. The organic matter in Norfolk fine sand was destroyed by burning in the muffle and boiling with conc. HNO_3-HCl. Three samples were treated with copper and washed in the same manner as the Eustis soil. The samples were each leached twice with 100-ml. portions of N $NaC_2H_3O_2$ having the pH adjusted with $HC_2H_3O_2$—sample 1 with solution at pH 4.2, sample 2 at pH 5.0, and sample 3 at pH 5.8. The third leaching for each sample was with N HCl. Although some copper is fixed by the sand, the amount is very small compared with that by the Eustis soil. There was obviously some variation in the amounts initially contained in each sample.

FIXATION OF COPPER BY NORFOLK FINE SAND

Of a 100-pound-per-acre application of copper to a hydrogen-saturated Norfolk fine sand, Peech (4) recovered only 40 per cent by a single salt extraction. When the soil pH was adjusted from 3.1 to 5.0, the recovery dropped to below 10 per cent and was correspondingly low for soil pH values of 6.0 to 8.0. At soil pH 6.0, only a small portion of a 300-pound-per-acre application was recovered. He also found that inorganic phosphorus appeared to have no relationship to copper fixation.

To check these results, samples of the same soil used by Peech were leached with 0.01 N HCl until some time after blank tests were obtained for phosphorus. After the samples were washed with about 200 ml. distilled water, however, the leachates became lightly yellow with dispersed humus. A positive test was obtained for phosphorus with this leachate before and after the removal of traces of silica and destruction of the organic matter. It appeared that although no free inorganic phosphates were left in the soils, phosphatic groups were attached to the organic colloids. Since it was still possible for this phosphorus to affect copper fixation, the following simple experiment was designed.

An iron hydroxide suspension was prepared from $FeCl_3$ and washed free of chlorides. Two 100-gm. hydrogen-saturated soil samples were added to 500-ml. volumetric flasks. To one of these and to an empty flask, 25 ml. of the iron suspension was added. Equal amounts of copper were added in solution to each of these flasks and to an additional empty flask. The addition of copper to the soil was equivalent to 300 pounds of copper to 2,000,000 pounds of soil (0.472 m.e. per 100 gm.). After standing overnight, sufficient NaCl solution was added to each flask to make the concentration 1 N at the final volume. After adjusting the pH to 4.0 with $HC_2H_3O_2$ and NaOH, the last few milliliters of water needed to make to volume were added to each flask. The suspensions were allowed to stand 24 hours before some of the supernatant liquid was siphoned from each. The copper in solution was estimated colorimetrically as the ammonium complex. The results are shown in table 4.

It appears that the presence of iron in this soil at a pH where it would tend to be active and tie up active phosphatic groups had no effect on the fixation of

copper. The presence of phosphatic groups in relatively small quantities in this soil has no measurable influence on its retention of copper. This is in agreement with the results of Peech (4).

With this soil, Peech recovered 17 per cent of a 100-pound-per-acre application at soil pH 4.0 and only a small fraction of a 300-pound-per-acre application at soil pH 6.0. In the present study, about 40 per cent of a 300-pound-per-acre application was recovered at solution pH 4.0. The recovery apparently increases more rapidly with increased application at pH 4.0 than at pH 6.0. With Norfolk sand previously used (free of organic matter but unground), recovery of a 300-pound-per-acre application was almost complete at solution pH 4.0 and 5.0. At pH 6.0 the recovery was only 33 per cent. From this and from the results shown in figure 2 for this sand, finely ground, we see that although finely divided quartz may fix copper at pH 5.0, the amounts are small as compared with those fixed by the natural soil. The fixation of copper in acid soils must be due to the formation of slowly soluble organic copper compounds. When the pH is

TABLE 4

Copper fixation by H-saturated Norfolk fine sand at solution pH 4.0

	Cu^{++} RECOVERED IN *N* NaCl	APPARENT FIXATION	CORRECTED FIXATION	PERCENTAGE FIXATION
	m.e./100 gm.	*m.e./100 gm.*	*m.e /100 gm*	
N NaCl + 100 gm. soil + 0.472 m.e. Cu^{++}	0.289	+0.183	0 187	39.6
N NaCl + 0.472 m.e. Cu^{++}	0.476	−0 004		
N NaCl + 100 gm. soil + 0 472 m.e. Cu^{++} + 25 ml. Fe $(OH)_3$ susp. ..	0 317	+0.155	0.191	40 5
N NaCl + 25 ml. Fe $(OH)_3$ susp. + 0 472 m.e. Cu^{++}	0.508	−0.036		

6.0 or above, copper fixation can be partly due to the precipitation of basic copper compounds.

CONCLUSIONS

The adsorption of copper from copper salt solutions by several sandy soils of Florida is found to be a function of copper concentration and only roughly related to the exchange capacities. Copper adsorption does not offer a reliable method for the determination of the exchange capacities of these soils.

The soils studied have a marked capacity to hold adsorbed copper in slowly replaceable as well as in slowly soluble forms. The distinction between fixed and exchangeable copper is not easily made. The recovery of copper by a single extraction with a replacing salt solution does not give a very reliable measure of fixation of copper in nonreplaceable forms. The copper removed after a somewhat drastic leaching with a salt solution appears to be related in part to the cation concentration.

There is evidence that copper can be mobilized in soil by the dispersive effect

of sodium salts on the organic colloids. Acetate is more effective than chloride in the solution of copper from soil.

Although phosphatic radicals capable of giving the molybdenum test were not removed by washing Norfolk fine sand with dilute HCl, the phosphorus retained apparently did not affect the retention of copper in the soil. The sand itself may retain some copper, but the amount is far less at pH 3 to 5 than that which can be attributed to the organic matter.

Time of solution contact influenced the retention of copper, but air-drying the soil gave no significant effect.

Since citrus trees are known to respond to moderate soil applications of copper sulfate (100 pounds Cu per acre) and since the copper is largely retained in slowly soluble or slowly replaceable forms, it appears that a small continuous supply in the soil may be more important than the amount of copper that is easily replaceable. An ordinary soil application of copper would doubtless be toxic were it not for its fixation.

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EXTRACTION OF AUXIN FROM VIRGIN SOILS

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Since auxins have been found in plant tissues it is reasonable to suppose that these materials may persist through certain stages of decomposition of organic matter in soils and thus become a part of the soil, or may indeed be synthesized during some part of the decomposition process. The data presented here are concerned with the presence of auxins in virgin soils and their relation to other soil characteristics. What this means in relation to plant growth is largely left for future consideration. It is possible that through a more thorough study of auxin some light may be thrown on one of the persistent problems of soil science: What influence, if any, does soil organic matter have upon plant growth aside from its recognized functions of furnishing plant nutrients and influencing the physical properties of soils?

THE AUXIN TEST

"Auxins" are defined (21) as "those substances that give curvature (*i.e.*, growth promotion by cell enlargement) in the standard *Avena* test." This term is used here, since the type of growth response measured is cell enlargement. A practical assay method for auxin is based upon the comparison of cell enlargement brought about by the auxin being determined, with that by a pure chemical auxin such as indole acetic acid.

In this report the standard Avena test (21) was used. This test derives its name from the fact that the growth response of 4-day-old oat plants is used as an indication of the cell enlargement (auxin) properties of the substance being tested. The principles and technique, which are frequently discussed in plant physiological literature, are briefly reviewed here. The basis of the test lies in the stimulation of growth on one side of the coleoptile over that on the other side. This increased growth on one side causes the coleoptile to curve. The curvature is proportional, within limits, to the amount of differential growth.

In the Avena test, the Victory strain of oats is used. The glumes are removed from the seeds, which are then soaked in water for 2 to 3 hours. They are then laid out on moist filter paper in moist chambers and allowed to germinate for 30 hours at 25°C. and 85 per cent humidity in a controlled room. Illumination in this room, when needed for working, is by means of a 100-watt Mazda light filtered through an orange-red Corning No. 243 filter. All test operations are carried out in this room. While the seeds are germinating they are continuously illuminated by a dim red light. This inhibits the growth of

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the mesocotyl, which if allowed to grow usually becomes curved and thus makes the plant unsuitable for use. At the end of the germination period the seeds are selected for uniformity of roots and coleoptiles and "planted" in small glass holders mounted in rows of 12 on wooden blocks. These holders are arranged vertically over troughs so that the roots may grow downward into the water. After 66 hours the coleoptiles are between 25 and 40 mm. long. In field-grown oats the coleoptile seldom appears much above the ground, as its elongation ceases when its tip is exposed to light. From the height of 3 or 4 mm. to its final size, the growth of the coleoptile is by *cell enlargement* only, not by cell division. The plants are next critically selected for uniformity of height and straightness. Two millimeters of each coleoptile tip is cut off by means of a razor, the plants are allowed to stand for 3 hours, and then a second decapitation is made to increase the sensitivity of the plants to auxin. Care is taken not to injure the tip of the leaf which is inclosed within the coleoptile. After the second decapitation, the leaf is broken away from its base by grasping the tip with forceps and pulling gently upward, until the leaf extends about a centimeter above the cut surface of the coleoptile. A small block (2 x 2 x 2 mm.) of 1.5 per cent agar is placed so that it rests on part of the cut surface of the coleoptile and with one side of the block against the leaf (fig. 1). (Had the leaf not been broken free of its base inside the coleoptile it would have continued growing and lifted the agar block off the top of the coleoptile.) If the agar block contains an auxin, the auxin will diffuse through the cut surface into the coleoptile, and induce the cells on the side below the agar to enlarge more rapidly than do those on the opposite side. This causes the coleoptile to curve away from the side to which the treatment was applied. An hour and a half after the application of the block, when cell enlargement is occurring at its maximal rate, the curvature is measured by making a shadowgraph on photographic paper. The growth responses are thus permanently recorded and the degrees of curvature may be easily measured with a goniometer. Up to 30° ("maximum angle") the curvature is linearly proportional to the concentration of auxin. At least 12 individual plants are averaged for each auxin determination. The standard error of the mean is about 10 per cent of the mean.

The sensitivity of Avena coleoptiles to a given amount of indole acetic acid may vary slightly from day to day. For this reason a standard control of 50 μgm. of indole acetic acid per liter is used simultaneously with tests of unknown samples, in order that the sensitivity of the coleoptiles for that day may be known. As with the samples being assayed, an average curvature of 12 control coleoptiles is taken. To facilitate comparison of determinations made with plants of different sensitivity on different days, the curvatures produced by the unknown samples are expressed in terms of the amounts of indole acetic acid that would be required to produce the same curvatures on the same day. These figures are designated as "indole acetic acid equivalents." It should be clearly understood that this is a comparative term and does not necessarily imply that indole acetic acid is the auxin being measured in the unknown samples.

EXTRACTION OF AUXIN

Methods used for the extraction of auxin from different kinds of substances have been of varied character, but freshly purified peroxide-free ethyl ether has been a popular solvent. This background of experience was utilized in the development of methods adapted to soil auxins. The surface horizons of Cecil,

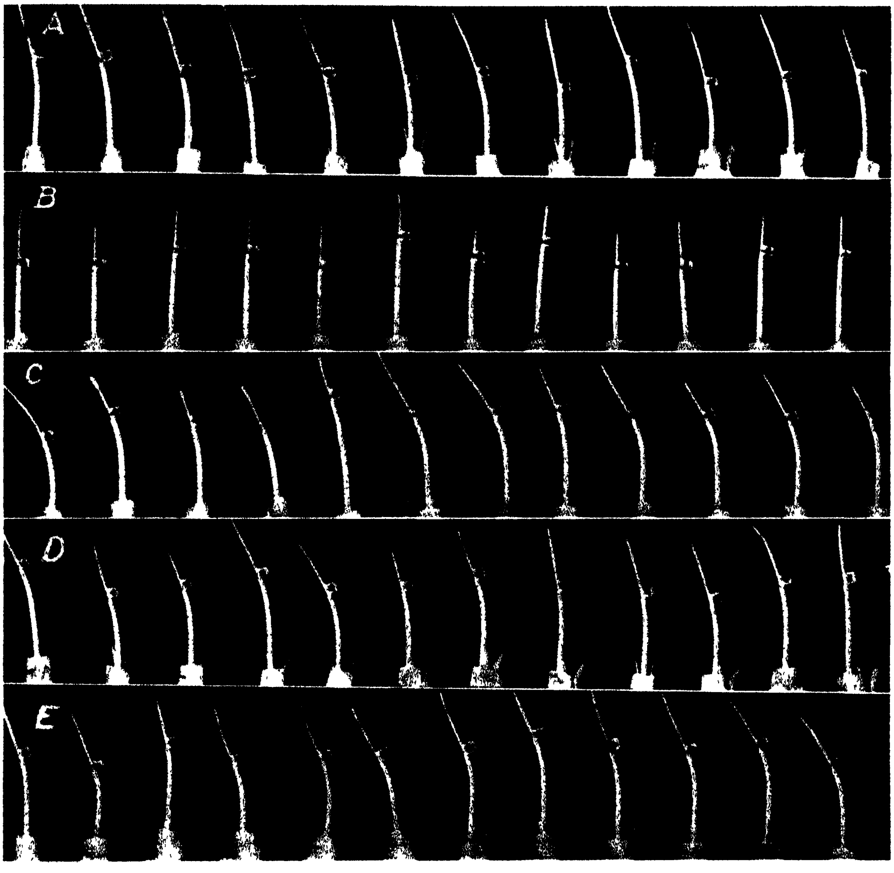

FIG. 1. CURVATURE OF AVENA COLEOPTILES IN RESPONSE TO AUXIN EXTRACTED FROM VIRGIN SOILS

A, Decatur, 0–12, and B, 12–36 inches, C, control, indole acetic acid, 50 μgm. per liter; D, Brookston, 0–6, and E, 6–20 inches

Russell, and Barnes soils were used in making a large number of preliminary experiments designed to find a suitable way by which to extract comparable quantities of auxin. Positive or negative results obtained by means of various methods of extraction led the work from step to step until a fairly acceptable procedure was found. A resumé follows:

Little or no auxin was extracted by shaking with ether or alcohol alone, at least from acid soils, and extracts with water alone gave variable results.

Acidifying to a pH of 4.5 with hydrochloric acid or acetic acid, with or without subsequent refluxing on an electric hot plate, gave no auxin in the water-ether extract.

Mixtures of ether and water extracted more auxin from acid soils than either solvent alone, but approximately the same amount was extracted by water as by ether-water mixtures when the soil was slightly alkaline.

Addition of calcium hydroxide solution to the soil and water mixture in sufficient amount to give a final pH of about 7.5 yielded the most consistent amounts of auxin of any method tried, and formed the basis of the method adopted. This method is described below.

One hundred grams of air-dry soil in an 800-cc. beaker was treated with 200 cc. of water, and enough limewater was added to produce a final pH of about 7.5. In acid soils this was an excess of about 30 per cent over that required to hold such a pH for the first 2 hours. Enough water was then added to make the total liquid volume 400 cc. After standing with occasional stirring for 48 hours, the total extraction period, the suspension was filtered on a Büchner funnel through No. 1 Whatman filter paper, and the filtrate evaporated to dryness in a casserole over a steam bath. Twelve cubic centimeters of water were then added, and the walls were carefully policed down. This solution was transferred to a 250-cc. wide-mouth Erlenmeyer flask and 120 cc. of ether added; the flask was stoppered, shaken at intervals, and stored in an icebox overnight.

The following day the ether was carefully decanted from the solution into another Erlenmeyer flask of similar size and evaporated on a water bath to 3 to 5 cc. This solution was then transferred dropwise by means of a pipette on 0.3 cc. of 1.5 per cent agar contained in a 5-cc. shell vial. To insure complete evaporation of the ether between drops, the vial was suspended in a rapidly boiling water bath. The Erlenmeyer flask was carefully rinsed twice with 2-cc. portions of fresh ether, which were similarly transferred to the agar. Then the walls of the shell vial were carefully washed down with fresh ether. By this procedure auxin from a 48-hour water extract of soil was concentrated in 0.3 cc. of 1.5 per cent agar. This volume of agar was molded into 12 blocks suitable for auxin determination by the Avena test. Inasmuch as the amounts of auxin obtained by this procedure caused Avena curvatures which were less than the maximum angle (30°), it was not necessary to make auxin determinations at dilutions of the original extract.

It should be borne in mind that failure to detect auxin by the method reported here does not necessarily mean that there was no auxin in the soil, but instead that the amount extracted was too small to cause a measurable curvature of the Avena. Since 0.025 μgm. indole acetic acid equivalent per kilogram of soil will give a measurable curvature, test samples which failed to give a curvature probably contained less than this amount.

SOILS USED AND THEIR AUXIN CONTENT

The soils selected for this investigation are samples of those used in other investigations by this Bureau. Some have been described in detail in previous publications, and detailed descriptions of others will appear later. General characteristics of most of the soils included are summarized in the 1938 Yearbook of the Department of Agriculture (19). The soils are typical

specimens of 11 soil series representing four of the great soil groups. Barnes loam from South Dakota is a chernozem, and Carrington loam from Iowa is of the prairie group. Five soils representing the gray-brown podzolic group include

TABLE 1

Relation of auxin to other properties in virgin soils

LABORATORY NUMBER	NAME AND LOCATION OF SOIL*	HORIZON	DEPTH	pH	ORGANIC MATTER† CONTENT	INDOLE ACETIC EQUIVALENTS PER KGM. OF SOIL	
						Sample 1	Sample 2
			inches		*per cent*	*μgm.*	*μgm.*
C2929	Barnes loam, S. D.	A	0–9	6.9	5.98	0.165	0.134
C2930		B_1	9–17	7.1	2.36	0.161	0.169
C4043	Brookston silty clay loam, Ind.	A_1	0–6	6.8	10.42	0.112	0.113
C4044		A_2	6–20	6.4	2.67	0.148	0.196
C2916	Carrington loam, Iowa	A_1	0–3	5.5	5.57	0.106	0.141
C2917		A_2	3–13	5.2	3.43	0.122	0.154
C4060	Miami silt loam, Ind.	A_1	0–2	6.3	6.22	0.084	...
C4061		A_2	2–5	5.9	3.60	0.034	....
C3174	Russell silt loam, Ind.	A_1	0–2	5.8	6.26	0.125	0.118
C3175		A_2	2–8	4.5	2.94	0.000	0.039
C 798	Hagerstown silty clay loam, Pa.	A_1	0–2	4.5	11.04	0.043	0.068
C 799		A_2	2–8	4.8	2.53	0.000	0.026
C4031	Hillsdale fine sandy loam, Mich.	A_1	0–3	7.5	4.28	0.118	0.072
C4032		A_2	3–9	7.5	0.72	0.000	....
C7178	Decatur silty clay loam, Ga.	A	0–12	6.3	4.05	0.132	0.100
C7179		B_1	12–36	5.7	0.46	0.000	0.026
C7173	Cecil fine sandy loam, S. C.	A_1	0–2	6.1	4.16	0.069	0.099
C7174		A_2	2–8	5.1	0.85	0.000	0.067
C7186	Georgeville silt loam, N. C.	A_2	½–5	4.5	3.44	0.097	0.092
C7187		B_1	8–28	4.7	0.23	0.000	0.000
C7190	Norfolk fine sandy loam, N. C.	A_1	0–2	4.4	10.52	0.038	....
C7191		A_2	2–13	5.3	0.43	0.000	0.000

* Soils arranged in order of approximate native fertility.

† Determined by combustion, $CO_2 \times 0.471$.

Brookston silty clay loam, Miami silt loam, and Russell silt loam, each from Indiana; Hillsdale fine sandy loam from Michigan; and Hagerstown silty clay loam from Pennsylvania. The red and yellow podzolic group is represented by Cecil fine sandy loam from South Carolina, Decatur silty clay loam from Georgia,

TABLE 2

Curvature of Avena coleoptiles in relation to auxin extracted from virgin soils

As degrees, and as micrograms of indole acetic acid equivalents per kilogram of soil, bracketed numbers

SOIL TESTED	HORIZON	DEPTH	DATE OF AVENA TEST							
			10-4	10-6	10-7	10-9	10-10	10-11	10-16	10-17
		inches								
Barnes, S. D.	A	0-9			22.6 [0.134]			17.6 [0.165]		
	B_1	9-17			18.5 [0.109]			18.0 [0.169]	20.1 [0.161]	
Brookston, Ind.	A_1	0-6	17.0 [0.112]			11.3 [0.113]			18.3 [0.147]	
	A_2	6-20		24.4 [0.196]		14.8 [0.148]			25.2 [0.202]	
Carrington, Iowa	A_1	0-3			17.9 [0.106]				17.6 [0.141]	
	A_2	3-13			20.5 [0.122]		24.7 [0.172]			22.0 [0.154]
Miami, Ind.	A_1	0-2								12.1 [0.084]
	A_2	2-5								4.9 [0.034]
Russell, Ind.	A_1	0-2			20.0 [0.118]					17.9 [0.125]
	A_2	2-8			0.00 [0.000]			4.2 [0.039]		
Hagerstown, Pa.	A_1	0-2	6.5 [0.043]				9.6 [0.068]			
	A_2	2-8	0.0 [0.000]				3.7 [0.026]			
Hillsdale, Mich.	A_1	0-3		8.8 [0.072]		11.8 [0.118]				
	A_2	3-9		0.0 [0.000]						
Decatur, Ga.	A	0-12		16.2 [0.132]			14.0 [0.100]			
	B_1	12-36		0.0 [0.000]			3.6 [0.026]			
Cecil, S. C.	A_1	0-2		8.4 [0.069]						14.2 [0.099]
	A_2	2-8			0.0 [0.000]	6.7 [0.067]				12.3 [0.086]

TABLE 2—*Concluded*

SOIL TESTED	HORIZON	DEPTH	DATE OF AVENA TEST							
			10–4	10–6	10–7	10–9	10–10	10–11	10–16	10–17
		inches								
Georgeville, N. C.	A_2	½–5		0.0 [0.000]				9.8 [0.092]	12.2 [0.097]	
	B_1	8–28		0.0 [0.000]				0.0 [0.000]		
Norfolk, N. C.	A_1	0–2	5.7 [0.038]							
	A_2	2–13	0.0 [0.000]				0.0 [0.000]		0.0 [0.000]	
Indole acetic acid, 50 μgm. liter			22.5	18.4	25.4	15.0	21.1	16.0	18.7	21.5

Georgeville silt loam from North Carolina, and Norfolk fine sandy loam from North Carolina.

Each soil was air-dried and passed through a 2-mm. sieve. The soils had been in storage from 3 months to 4 years. Data taken for these soils according to the procedure described above are given in table 1. In this table also are given the original pH values and organic matter contents of the soils used. In table 2 more detailed data obtained in the Avena test are given.

The soils included in tables 1 and 2 are listed in the order of their approximate native fertility. It is recognized that no accurate basis exists for making such a comparison when areas are widely removed from one another. This listing should be considered as having only general significance. The data in these tables, together with various preliminary results not given in detail, show several general relationships:

The extractable auxin content tends to decrease with increasing soil acidity.

Surface and second horizons of soils of excellent native fertility tend to have higher extractable auxin contents than do the second horizons of less fertile soils. It may be that the auxin content is influenced by kind as well as quantity of organic matter present.

It is recognized that determination of the auxin content of soils by the procedure described does not possess the same degree of precision as is involved in the determination of most of the inorganic chemical constituents. It is not known what part of the auxin present is extracted by the means used, nor is it known to what extent, if any, auxin is created or destroyed by the extraction process that was carried out under nonsterile conditions. The important fact is that fairly concordant duplicate determinations were obtained when extractions were made at different times and evaluated with different sets of oat plants separately standardized as to sensitivity to auxin.

NATURE AND SIGNIFICANCE OF AUXIN

A publication by Parker-Rhodes (12) constitutes the only previous work on determination of auxin in soil. This author, working on cultivated soils in England, estimated the amounts of auxin by a root-hair plasmolysis technique. In terms of indole acetic acid, auxin concentrations of 10^{-9} to 10^{-10} moles per kilogram of soil are reported. These figures are in close agreement with the present data obtained by the standard Avena test. He also suggested that auxin from soil has certain characteristics of indole acetic acid.

From auxin determinations of soil microorganisms, Roberts and Roberts (13) conclude that the soil flora is potentially capable of producing appreciable amounts ofa uxin. The work of Kögl and Kostermans (6), Thimann (16), and others indicates that the auxin produced by many of these microorganisms is indole acetic acid.

At present the chemical compound or compounds acting as soil auxin(s) are unknown. Refluxing with acid brought about destruction of soil auxin properties, and in this respect the substance behaved like indole acetic acid. On the other hand, it was not extractable directly from the soil with ethyl ether, as indole acetic acid would probably have been, unless the presence of soil interferes with such extraction.

It is generally thought that no external supply of organic substance is essential for growth of green plants, although the presence of such organic compounds as artificially prepared humates may be beneficial in water or sand cultures, as carriers of available iron. Perhaps in some other manner, not now understood, certain organic compounds in the soil stimulate plant growth. Now that means are available for measuring amounts of soil auxin it would be interesting if it develops from further research that auxin could cause such stimulation. Thus it would be possible to detect auxin-deficient soils and perhaps develop techniques to supply this deficiency. Though there actually are claims that indole acetic acid and other auxins added to soil, some by seed treatments, stimulate growth (3, 5, 9, 10, 14, 18, 20), there are nearly as many claims that this is not so (4, 7, 11, 15). The present data, of course, make no case for the desirability of adding auxin to soil as a means of stimulating plant growth, but they show that naturally fertile soils do tend to contain more auxin than less fertile ones, and the less fertile surface soils more than their subsoils. Thus it is possible that natural soil auxin may have some stimulative effect upon plant growth. Also, it may help to explain the well-known infertility of subsoils.

Comparison may be made of the concentrations of auxin in fertile soils with those reported to have a stimulating effect on root growth. Amlong (1) has reported that application of 10^{-9} molar indole acetic acid solution to roots the tips of which were excised; results in a slight but very definite root growth increase. Others investigators have reported similar effects for the same concentration (2, 17). Indole acetic acid 10^{-9} molar (0.175 μgm. per liter) is approximately the same as the concentration of auxin extractable from fertile soils (table 2). It may be that one of the contributing factors to the fertility

of these soils is their near optimal auxin concentration for root growth. Furthermore, the pH of these soils should not be destructive to auxin, as one would expect a more acid soil to be.

Recently Laude (8) has shown that a 10^{-9} molar solution of indole acetic acid when applied to tomato plants grown in washed quartz sand, with added inorganic nutrients, increased the dry weight 12.5 per cent more than that of control plants receiving the inorganic nutrients alone. Again the concentration of auxin in the fertile soils seems to approach this optimum.

At present, interest in auxins centers primarily around a few definite chemical compounds of proved auxin activity. There is, of course, no way of knowing how many more organic compounds not yet discovered may have auxin effects. Most of the problems associated with auxins in soils that come to mind remain to be solved. Among these are the following: Are there different optimal auxin concentrations for the growth of different plants? Do natural bodies in soils other than the known auxins produce similar physiological effects, and what is their chemical nature? What are the effects of liming on soil auxin? What role does soil flora have in auxin production? Does auxin stimulate the growth of certain kinds of plants and not of others?

SUMMARY

A proximate method is described for the extraction and assay of auxin in soils. One hundred grams of soil is shaken at intervals for 48 hours with sufficient limewater to keep the pH between 7.0 and 8.0 in a volume of 400 cc. The filtered extract is then concentrated and auxin measured by the standard Avena test.

Auxin determinations were made on the two upper horizons of 11 virgin soils representative of four of the great soil groups.

In very fertile midwestern surface and subsurface soils auxin was found to the extent of about 0.175 μgm. per kilogram of soil (indole acetic acid equivalents). In the less fertile soils, considerably less auxin was found in the surface horizons and little if any in the second horizon.

The presence of auxin in soil as yet has not been generally conceded to be beneficial for plant growth. Its greater abundance in the more fertile surface soils, and its near absence in poor soils of low organic matter content, however, point to its possible association with soil fertility.

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BORON CONTENT OF HICKORY AND SOME OTHER TREES

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Recently McHargue, Hodgkiss, and Offutt[2] published a number of determinations of boron in various plants and plant parts. A sample of hickory leaves gathered late in the fall contained 160 p.p.m. of boron, which is considerably more than any other land plant contained. A boron determination by the same authors on hickory leaves gathered in the spring from a tree growing on a similar soil in a different location shows 59 p.p.m. There is no way of knowing whether this large difference in boron content is due to differences in soil composition or to seasonal variation. McHargue *et al.* refer to the work of Scribner,[3] who reported finding rare earths in the leaves of a hickory tree growing on a pegmatite vein near Amelia, Virginia. According to McHargue *et al.*, "These findings indicate that the mineral content of hickory leaves may vary considerably with the soil on which the trees grow."

Data recently submitted for publication elsewhere show that soils low in acid-soluble boron produce plants showing boron deficiencies and also that such plants are lower in boron than normal plants.

In a study of the distribution of boron in soils and plants, we have made boron determinations on a number of tree leaves. These determinations yield some evidence on the points raised by McHargue, Hodgkiss, and Offutt.

The leaf samples were gathered from several parts of the trees exposed to sun and wind, preferably on the south side.[4] The dried samples weighed from 1 to 5 kgm. It is believed that the taking of such large samples insures a fairly representative sample. The large stems of the compound leaves of hickory, locust, ash, and black walnut were removed. The difficulty of gathering these leaves in quantity from a precarious perch near the top of a tree made this removal necessary to ensure comparative samples.

The boron determinations were made according to the method of Wilcox.[5] Briefly, this method consists in ashing 10 gm. of the dried plant matter with calcium oxide at a low temperature. The ash is leached with water, the phosphates, etc., are precipitated in the lead nitrate, and the boron in solution is titrated electrometrically after the addition of mannite. Acid-soluble boron

[1] Senior chemist and assistant chemist, respectively, Bureau of Plant Industry.

[2] McHargue, J. S., Hodgkiss, W. S., and Offutt, E. B. 1940 The boron content of some important forage crops, vegetables, fruits and nuts. *Jour. Amer. Soc. Agron.* 32: 622–626.

[3] Scribner, B. F. 1939 Spectroscopic detection of rare earths in plants. *Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications*, p. 10–13. Wiley & Sons, New York.

[4] The hickory and sweet leaf samples from Gainesville, Florida, were gathered under the direction of R. V. Allison. The tung leaf samples were collected by M. Drosdoff.

[5] Wilcox, L. V. 1940 Determination of boron in plant material. *Indus. and Engin. Chem., Analyt. Ed.* 12: 341–343.

determinations in a few of the soils on which the leaves were grown were made by the method described by Whetstone, Robinson, and Byers.[6] The results are given in table 1.

The data of table 1 indicate that the boron content of leaves increases with the age of the leaf. This has been shown in the case of boron injury to citrus trees.[7]

Table 1 shows hickory leaves from hickory tree 4 to have the highest boron content of the leaves examined. This tree, however, was on the edge of a garden to which boron in the form of borax and ground Pyrex glass had been sparingly applied. The other hickory trees from Falls Church, Virginia, were on a lawn to which no boron had been applied. If we except hickory tree 4, two tree leaves, one black locust and the other black walnut, are higher in boron than the hickory leaves of table 1. The relative uniformity of boron content of the mature leaves of hickory trees 3 and 5 and of tree 3, taken on two different years, indicates that hickory tree leaves growing on the same soil are uniform in composition and also that mature leaves grown during different years are comparable. Only one tree leaf, tung from Gainesville, Florida, which contained 84 p.p.m. boron, has a higher boron content than the highest untreated hickory.

The boron contents of turnips and tomatoes are about the same as those found by McHargue *et al.* in these vegetables raised in Kentucky. The two instances where boron was determined in different parts of the same plant show that boron is concentrated in the leaves of the lima bean and the tomato and is low in the seeds and fruit.

It is believed that much of the difference in boron content of the two samples of hickory leaves given by McHargue *et al.* may have been caused by the difference in the time of sampling. It appears that differences in the boron content may amount to almost twice as much in samples taken in late fall as in early spring samples (see table 1). It is probable, however, that there was more available boron in the soil producing the hickory leaves of the highest boron content reported by McHargue *et al.*

Considerable importance is to be attached to the statement quoted earlier, that "these findings indicate that the mineral content of hickory leaves may vary considerably with the soil on which the trees grow." Data soon to be published from this laboratory show a rough relationships between the barium content of hickory leaves and the exchangeable barium in the soil. The analysis of forty samples of hickory leaves and soils from widely distributed localities for rare earths also shows a general dependence of the composition of one upon the other. Data which are now being assembled for publication show that the hickory is a heavy and variable feeder upon other inorganic elements. The aluminum content has been found to vary from less than $\frac{1}{4}$ to 2 per cent.

[6] Whetstone, R. R., Robinson, W. O., and Byers, H. G. 1942 Boron distribution in soils and related data. U. S. Dept. Agr. Tech. Bul. 797.

[7] Scofield, C. S., and Wilcox, L. V. 1931 Boron in irrigation waters. U. S. Dept. Agr. Tech. Bul. 264.

TABLE 1

Boron content of hickory and some other leaves and plant parts

Analyses of leaves only, unless otherwise indicated

KIND OF LEAVES OR PLANT PARTS AND LOCATION	DATE GATHERED	BORON	SOIL	ACID-SOLUBLE BORON IN SOIL
		p.p.m.		*p.p.m.*
Hickory, tree 3, Falls Church, Va.	June 1, 1940	32	Chester loam	7.0
Hickory, tree 3, Falls Church, Va.	July 5, 1940	39	Chester loam	7.0
Hickory, tree 3, Falls Church, Va.	October 1, 1940	52	Chester loam	7.0
Hickory, tree 3, Falls Church, Va.	September 25, 1939	51	Chester loam	7.0
Hickory, tree 4, Falls Church, Va.	October 14, 1939	93	Chester loam	(Boron added, see text)
Hickory, tree 5, Falls Church, Va.	October 15, 1939	55	Chester loam	7.0
Black locust, Falls Church, Va	October 6, 1940	30	Chester loam	7.0
Apple (Grimes Golden), Falls Church, Va.	October 1, 1940	37	Chester loam	7.0
Asparagus (stem, leaves, and immature seeds), Falls Church, Va.	June 7, 1939	9	Chester loam	7.0
Garden pea vines (in blossom), Falls Church, Va.	October 14, 1939	17	Chester loam	7.0
Turnip leaves, Falls Church, Va	October 14, 1939	26	Chester loam	7.0
Turnip roots, Falls Church, Va.	October 14, 1939	25	Chester loam	7.0
Pole lima beans, Falls Church, Va.	October 14, 1939		Chester loam	Soil above, to which about 3 lbs. B per acre was added
Mature seeds		8		
Stems		11		
Leaves		30		
Blossom clusters including stems and very small pods		24		
Immature pods and seeds		11		
Tomato, Falls Church, Va	August 31, 1939		Chester loam	Soil above, to which about 3 lbs. B per acre was added
Leaves		49		
Fruit		15		
Upper stems		25		
Table beets, Falls Church, Va.			Chester loam	Soil above, to which about 3 lbs. B per acre was added
Leaves		44		
Roots		20		
Hickory (Glabre), Gainesville, Fla.	June 1940	33	Arredonda fine sand	0 8
Hickory (Glabre), Gainesville, Fla.	December 1940	59	Arredonda fine sand	0.8
Sweet leaf (Symplocos Tinctoria), Gainesville, Fla.	June 1940	23	Arredonda fine sand	0.8
Sweet leaf (Symplocos Tinctoria), Gainesville, Fla.	December 1940	28	Arredonda fine sand	0.8
Tung tree (good growth), Gainesville, Fla.	October 1940	84	Arredonda sandy loam	3.9
Tung tree (poor growth), Gainesville, Fla	October 1940	45	Fellowship fine sandy loam	1.3
Black walnut, Catlett, Va.	June 9, 1939	40	Alton silt loam	19.2
Black walnut, Catlett, Va.	September 1939	67	Alton silt loam	19.2
Red ash, Catlett, Va	September 1939	59	Alton silt loam	19.2
Hickory, Edgewood, Md	July 5, 1939	18	Sassafras gravel	
Hickory, Edgewood, Md	September 30, 1939	31	Sassafras gravel	.
Hickory, White Oak, N C.	June 10, 1940	23	Cecil clay	4.4
Hickory, White Oak, N. C.	October 1941	45	Cecil clay	4.4
Hickory, Hagerstown, Md.	August 15, 1937	58	Hagerstown stony loam	14.3
Black locust, Hagerstown, Md.	August 15, 1937	77	Hagerstown stony loam	14.3
Hickory, Big Savage Mt , Md.	August 15, 1937	64	Frostburg podzol	5.5
Black locust, Big Savage Mt., Md.	August 15, 1937	44	Frostburg podzol	5.5
Hickory, Blackford, Va	June 13, 1940	23	Frederick silt loam	6.5
Black locust, Blackford, Va.	June 13, 1940	32	Frederick silt loam	6.5
Hickory, Amelia, Va..	June 15, 1937	41	Pegmatite vein soil	.
Hickory, near Waterloo, Iowa	June 2, 1941	21	Carrington loam	6.3
Rabbit grass, near Carlsbad, N. Mex.	November 1940	40	Red sandy soil	6.5
Creosote bush, Carlsbad, N. Mex.	November 1940		Red sandy soil	
Leaves		42		6.5
Small stems		30		6 5
Mesquite, Carlsbad, N. Mex.	November 1940	50	Red sandy soil	6.5
Sagebrush, includes small stems and seeds, Carlsbad, N. Mex.	November 1940	38	Red sandy soil	6.5
Rubber tree, Honduras Experiment Station	November 1940	53	Lancetilla silt loam	4.0
White birch, Hebron, Maine	August 1935	41		....
Rhododendron, Red Bank, N. C.	June 12, 1940	39		....

The manganese content varies from a trace to nearly $\frac{1}{2}$ per cent. These variations are in general dependent upon soil composition.

Because of the variable composition of its leaves, the hickory tree is a very useful indicator of available inorganic elements. It is widely distributed from Maine to Florida and westward to Iowa. The leaves are far less liable to soil contamination than most plants, a very serious objection to broad-leaved, low-growing plants such as beans. This objection applies to all cultivated plants and is serious with respect to the elements which occur in the plant in very small quantities but which make up the bulk of the soil.

PLANT NUTRITION AND THE HYDROGEN ION: I. PLANT NUTRIENTS USED MOST EFFECTIVELY IN THE PRESENCE OF A SIGNIFICANT CONCENTRATION OF HYDROGEN IONS

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The increasing recognition of the fact that the entrance of the hydrogen ion into the soil is the approximate reciprocal of the exit therefrom of calcium and other nutrient cations, might lead us to believe that complete removal of the hydrogen ion by cation restoration should be good soil management. Almost legion are the determinations of the pH of the soil to leave the inference that a significant degree of soil acidity is associated with low productivity. Application of limestone for hydrogen-ion removal from the soils in the humid region has become so general as a farm practice that it is approaching a crusade against soil acidity.

In most studies designed to determine the detrimental effect of a low pH on the various soil processes and on the summation of these processes as production of crops, the relations have too often been qualitative rather than distinctly quantitative. More recently, numerous exceptions have crept into the generalization that soil acidity is detrimental to crop quality or crop yield. That such a generalization might be untenable is suggested when we note that the maximum human population has come to support itself in the humid temperate zone, where food production, in consequence, must be high; yet it is in this region that the clay fraction of the soil is of such type as to permit the largest relative hydrogen adsorption and therefore the highest degree of soil acidity. If cognizance is taken of the evolutionary aspect of crop adaptation to this environment, most plant species have long been growing on soils with hydrogen present on the soil complex.

The very process of soil development, with carbonic acid as the dominating agency, demands an active role by hydrogen ions in the process and anticipates an end-product containing them. Should it not be a fair assumption, then, that the plant root itself has been evolved as a physicochemical system in approximate equilibrium with an environment representing some significant concentration of hydrogen ions? Since the examples of crop detriment by soil neutrality are accumulating, it would seem reasonable to believe that the movement of nutrient ions from the soil into the plant—and therefore plant growth itself—is at an optimum in the presence of at least some significant degree of hydrogen-ion concentration. The following study presents some evidence in support of this hypothesis.

[1] Professor of soils and assistant professor of horticulture, respectively. Contribution from the departments of soils and horticulture, Missouri Agricultural Experiment Station, Journal Series No. 784.

HISTORICAL

Calcium adsorbed on the colloidal complex of the soil is displaced, by simple chemical exchange, to a higher degree when it is associated with hydrogen than when associated with corresponding equivalents of barium, magnesium, or sodium, according to Jarusov (7). That this increased calcium activity in the presence of hydrogen is transmitted to plant growth activity is suggested in some work by Gedroiz (4). He points out that "in a soil fully saturated with hydrogen, the oats did not develop at all in the absence of calcium carbonate. Two causes prevented their growth; the absence in such soil of available calcium, and the acid reaction." Of his tests with the same soil saturated completely with each of the separate sixteen cations by a method that allowed the growth of oats, he remarked, "The crops gave the same yield as in the original chernozem only in the soil saturated with calcium." According to him, complete calcium saturation was no disturbance in terms of crop yields. He reports further, "The plants did not grow at all in the soils saturated with each of the remaining bases (except strontium) both without fertilization, and with nitrogen and phosphorus fertilizer. When, however, calcium carbonate was added to the soil, in addition to nitrogen and phosphorus, a normal crop similar to that on the original soil, was obtained only in the soil saturated [originally] with the hydrogen ions." According to him, then, the small amounts of calcium carbonate, of nitrogen, and of phosphorus were effective for normal plant growth when added to a soil originally saturated with hydrogen but not when put on a soil that was saturated with any other cation maintaining these soils neutral in reaction. This suggests therefore that, in terms of plant growth, calcium is as effective in small amounts and in the presence of hydrogen ions as it is in large amounts represented by clay saturation with it and consequently in the absence of hydrogen ions.

That calcium is more active when associated with hydrogen and its acidity than with barium and its neutrality is indicated by the work of Hutchings (6). Using colloidal clay as a nutrient medium to provide varying total amounts of calcium and varying degrees of saturation by either hydrogen or barium accompanying the calcium he has shown that significantly larger amounts of calcium and higher percentages of that exchangeable from the soil moved into the soybean crops when it was accompanied by hydrogen than by barium. Portions of his data are assembled in table 1.

In general, the soybean crops carried a higher calcium concentration and a higher total calcium content, and used the exchangeable calcium with a greater efficiency when this nutrient adsorbed on the clay was accompanied by hydrogen rather than by barium.

In a similar study, Horner (5) provided constant total amounts of exchangeable calcium at varying degrees of calcium saturation and reciprocally varying degrees of saturation by either hydrogen or barium. Portions of his data are assembled in table 2.

Again according to Horner's data, there were larger concentrations of calcium within the plants, larger total amounts taken by the crops, and a greater relative

TABLE 1

Calcium contents of the soybean crops according as hydrogen or barium was associated with the calcium on the colloidal clay

Data from Hutchings

DEGREE OF SATURATION BY		CALCIUM IN THE CROP		
Calcium	Reciprocal	Concentration	Total	Efficiency
		per cent	*mgm.*	*per cent*
Calcium and hydrogen				
	(Hydrogen)			
25	75	0.27	40.27	40.2
50	50	0.55	85.54	40.7
75	25	0.77	122.40	40.8
Calcium and barium				
	(Barium)			
25	75	0 29	31.20	31.2
50	50	0.31	45.54	22.7
75	25	0.66	104.84	34.9

TABLE 2

Calcium contents of the soybean crops according as hydrogen or barium was associated with constant total amounts of exchangeable calcium but varying degrees of saturation of the colloidal clay

Data from Horner

DEGREE OF SATURATION BY		CALCIUM IN THE CROP		
Calcium	Reciprocal	Concentration	Total	Efficiency
		per cent	*mgm.*	*per cent*
Calcium and hydrogen				
	(Hydrogen)			
40	60	0.507	25.2	12.6
60	40	0.651	44.8	22.4
75	25	0.702	50.9	25.4
87.5	12.5	0.764	57.1	28.5
Calcium and barium				
	(Barium)			
40	60	0.386	23.9	11.9
60	40	0.594	38.0	19.0
75	25	0.672	47.0	23.5
87.5	12.5	0.707	56.2	28.1

utilization by the crop of the constant amount of exchangeable calcium offered in every case where calcium was associated with the hydrogen ion rather than with the barium ion.

According to these data by Gedroiz, by Hutchings, and by Horner, the greater utilization by the plant of calcium when associated with hydrogen rather than with barium, or other cations, is in agreement with the simple chemical behavior suggested by Jarusov. Since the plant behavior is in agreement with the chemical behavior, the failure of the plant to absorb as much calcium when this is associated with barium as when associated with hydrogen, seems less a case of so-called barium "toxicity." It is highly suggestive that it represents increased calcium activity through its association with hydrogen, whether in soil-plant performances or in the laboratory test tube.

PLAN AND METHODS

If the hydrogen ion exerts beneficial effects in "mobilizing" calcium into legumes, which are considered calcophiles—or what has been more commonly interpreted as "acidophobes"—might not the hydrogen of the soil be an agent helping nonlegumes to obtain ample calcium from the soil by making the small supply more active toward entrance into the crop? In order to test this question, spinach and potatoes, both nonlegumes of dietary importance, were selected. The former was chosen in consideration of its extensive garden use without regard to soil requirements, its general inclusion as a leafy green vegetable in recommended diets for its mineral contents of antirachitic value, and the controversial value of its calcium content as related to the extent of possible precipitation of calcium within the plant as an oxalate. The potatoes were chosen because of the commonly recommended practice that they be grown on acid soils.

The soil for spinach production was prepared in an attempt to supply all the required nutrients accompanied by (*a*) significant amounts of hydrogen, or in a soil at pH 5.2 (as determined by means of the glass electrode), and (*b*) almost no hydrogen, or in the same soil at pH 6.8. In the following discussion, the former will be considered as the "acid" series and the latter as the "neutral" series. Additions of calcium to the soil were varied by increments of 3 m.e. per plant, through a series from 0 to 12 m.e., in order to study the influence of the variation of amounts of this nutrient in the presence or absence of the hydrogen ion. The other nutrient additions to the soil were constant and included 3 m.e. of magnesium, 6 m.e. of potassium, and 6 m.e. of phosphorus. The soil was given the amounts of cations and anions as set forth in table 3.

The soil given these modifying treatments was an acid, clay subsoil of Putnam silt loam. This clay had a total exchange capacity of 28 m.e. per 100 gm. Of this capacity, 12 were taken by calcium, 12 by hydrogen, and 4 by other cations. The original soil thus carried exchangeable calcium to the extent of 43 per cent of possible saturation. The additions of calcium did not carry the total exchangeable calcium beyond 67 per cent of saturation. The total amounts of all cations added were such as should have been completely adsorbed on the colloidal complex.

In providing the soil with variable calcium levels but of neutral reaction, the cations were added mainly as oxides and hydroxides. The additions of the amounts indicated in table 3 resulted in a soil with a pH of 6.8.

In providing the soil with variable amounts of calcium but of acid reaction, the cations were added as neutral salts according to the amounts in table 3. This acid soil carried, therefore, such anions as nitrates, chlorides, and sulfates. No acid was added, but these additions of salts resulted in a pH of 5.2. Lesser amounts of clay were used in preparing this acid series than the neutral series; hence less of the original soil calcium was offered in the former than in the latter series, as shown in table 3. At any single calcium level, the difference in amount of soil between the acid and the neutral soil was no greater than 50 gm. With no calcium applied, the difference was no greater than 35 gm., as contrasted to the maximum total amount of soil at 225 gm. per pot.

Because of the variable amounts of clay, the increase of which made possible the provision of the increasing amounts of calcium while adding constant

TABLE 3

Nutrients added to the soil to provide variable calcium levels under low and high pH levels

	NUTRIENTS PER PLANT							CLAY PER PLANT	RESULTING pH
	Ca	N	P	K	Mg	S	Cl		
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*gm.*	
Low pH, or "acid" soil..	0	6	6	6	3	3	2	91.5	5.2
	3	6	6	6	3	3	1	100.0	5.2
	6	6	6	6	3	3	2	125.0	5.2
	9	6	6	6	3	5	3	150.0	5.2
	12	6	6	6	3	9	4	175.0	5.2
High pH, or "neutral" soil	0	6	6	6	3	3	.	125.0	6.8
	3	6	6	6	3	3		150.0	6.8
	6	6	6	6	3	3		175.0	6.8
	9	6	6	6	3	3		200.0	6.8
	12	6	6	6	3	3		225.0	6.8

amounts of the other cations, a variation in the degree of saturation by the different cations naturally resulted. The saturation degree for calcium increased with increasing amounts of clay from 43 to 67 per cent for the acid series and from 43 to 62 per cent for the neutral series. The saturation degrees for the potassium and the magnesium decreased with increasing amounts of clay. For the former the shifts were from 23 to 12 per cent and from 17 to 9.5 per cent for the two series respectively. For the latter the figures changed from 11 to 6 and from 8.5 to 4.7 per cent accordingly. Thus while the saturation for calcium was increasing in the series, it was decreasing for potassium and magnesium. These variable amounts of clay were of no significance in disturbing the texture of the sand-clay mixture in which they were used to fill the pots. In all instances, the mixture was of a sandy texture with decided dominance of sand.

Whether the cations in the acid soil with their accompanying different anions have the same relation to the plant as when the cations were applied principally as oxides or hydroxides, involves the questions of their degree of adsorption and of their presence possibly in solution within the soil. The sulfate ion was used

in both the neutral and the acid soil, though in larger amounts in two cases of the latter. The chloride and the nitrate anions were present at the outset only in the acid soil. Nitrogen, representing both cation and anion forms, in ammonium nitrate was added during the growth of the plants on both the neutral and the acid soils. This amounted to 3.5 m.e. of each ion form, or a total of 7 m.e. of nitrogen. With the consumption of the nitrate ion by the plant, this removal should tend toward the induction of alkalinity. The chloride ion was, therefore, in the main, the differing ion between the neutral and the acid soils. Since variable amounts of this anion were used even within the acid soil series, variations in plant response in accordance with them should be manifest if the chloride ion is a significant factor.

These variations in anions between the acid soil and the neutral soil are an inescapable experimental condition, since the introduction of acidity is impossible when the amounts of cations are held constant without the incorporation of the anions. Such is the occurrence in practice where the application of fertilizers involves the use of salts, hence the conditions were accepted for experimental purposes in these trials. As the data reveal, no significant influence could be ascribed to any of the individual anions introduced as possible irregularities into the plan of the experiment.

The variety of spinach used was Bloomsdale Long-standing. Four seeds per 5-inch clay pot were planted and thinned later to one plant per pot. Forty plants represented each of the ten different treatments. The season of growth extended from February 10 to April 15. The usual careful control of greenhouse conditions was maintained. The tops of the plants were harvested, washed, dried at 65°C., weighed, and ground for chemical analyses.

The soil for the potato production was prepared in the same manner as that used for the spinach. The same two degrees of hydrogen-ion concentration, namely, pH 5.2 and 6.8, were used. In these, however, the amount of treated clay taken was larger than that used for the spinach in order to accommodate the larger potato plants. In both series, the allotment of potassium was a constant at 60 m.e. per plant, whereas the calcium was used at 30, 60, and 90 m.e. The amounts of the other elements were also larger, as represented by 60 m.e. each of nitrogen and of phosphorus, and 6 m.e. each of magnesium and sulfur per plant.

An additional potato series at pH 5.5 was introduced in order to test the influence of a wider variation in the amount of potassium through 10, 50, and 100 m.e. per plant when the calcium was held constant at 60 m.e. All other nutrient levels in these series were the same as in the other series for potatoes.

These three series with the potatoes permitted observation of pathological behaviors manifested by the incidence of potato scab as premised on controlled physiological conditions.

The variety of potatoes used was the Red Warba. Uniform apical cuttings of 1½–2 ounces in weight were used as seed stock in the soils at pH 5.2 and 6.8. Basal cuttings of the same size served in the series at pH 5.5. The season of potato growth extended from March 10 to May 15, or a total growth period of 66 days.

EXPERIMENTAL RESULTS

Yield of crops

The weight of the spinach crop produced was larger, in general, on the soil nearer the neutral point than on the acid soil throughout the series of calcium increments, except where 9 m.e. was applied.[2] For the neutral series this was a relative decline in the curve, as shown in figure 1. There was also one recession in the corresponding curve for the acid soil, but this occurred where 6 m.e. of calcium was added. The summation of all the dry crop weights of the entire series on the acid soil gave 259 gm. The corresponding figure for the neutral soil was 279 gm. Since 200 plants were involved in each series, the difference

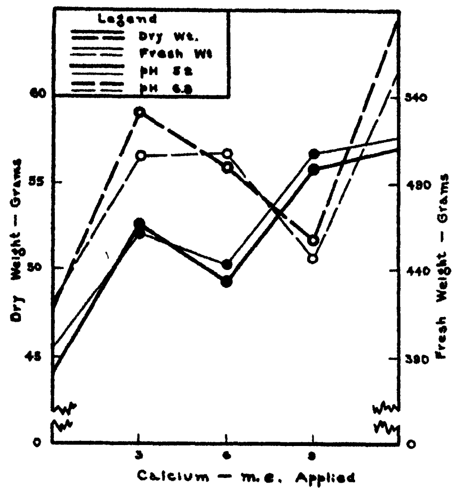

FIG. 1. WEIGHTS OF SPINACH IN RELATION TO EXCHANGEABLE CALCIUM APPLIED TO SOIL AT DIFFERENT DEGREES OF ACIDITY

in weights amounts to 0.1 gm. per plant increase over a mean individual plant weight of 1.295 gm., or an increase of 7.8 per cent because of the neutral soil.

These effects of the increasing amounts of calcium offered within each series are also reflected by increased crop yields. The crop yield for the maximum calcium addition was greater by 12.96 gm. than that of the no-calcium treatment in the acid soil series. The corresponding spread in yield was 15.90 gm. in the neutral soil. The figures represent yield increases in consequence of calcium additions, of 29 and 33 per cent, respectively, over the soil given the same other nutrient additions but no calcium. Though the yield increases due to calcium increments were not straight-line functions of these, all calcium treatments, regardless of amounts, resulted in yield increases of the spinach crop.

The weights of the potato crop are given in terms of the yield of tubers and of tops in table 4. It is significant that the potato crop—quite the reverse of

[2] The complete data as to crop yields and chemical composition have been assembled elsewhere (8).

spinach—was greater on the acid soil at pH 5.2 than on the more nearly neutral soil at pH 6.8. A total of 622 gm., dry weight, of tubers was produced by the soil at pH 5.2 with the three different calcium levels, and only 543 gm. with the same potassium-calcium series at pH 6.8. This is an increase of 14 per cent as a result of the presence of more hydrogen in the soil medium. It is significant that the yield of tops, also, was 28 per cent higher as the result of the more acid reaction in the soil.

The yields at pH 5.5 are not strictly comparable with the others because they were from plantings of only basal pieces. Nevertheless, they illustrate a growth equivalent of that on the soil with the reaction of pH 6.8, even though the potassium applications in two of the three cases were lower than those on any of the other trials. This suggests a high degree of efficiency for the lower potassium supply on the soil with this low figure for pH.

TABLE 4

Yields of potatoes, tubers and tops, and the numbers of scab areas in relation to variable calcium with constant potassium and vice versa at different degrees of soil acidity

DEGREE OF ACIDITY	APPLICATIONS OF		YIELDS, DRY WEIGHT		SCAB AREAS
	Calcium	Potassium	Tubers	Tops	
pH	*m.e.*	*m.e.*	*gm.*	*gm.*	
5.2	30	60	224	58	42
	60	60	200	58	6
	90	60	198	58	19
6.8	30	60	181	44	41
	60	60	192	47	8*
	90	60	170	45	46†
5.5	60	10	137	29	9
	60	50	234	46	20‡
	60	100	175	44	84§

* Two potatoes had one fourth of their entire surfaces covered with scab.

† One potato had half of its entire surface covered with scab.

‡ One potato had one third of its entire surface covered with scab.

§ Two potatoes had their entire surfaces covered with lesions.

Plant composition

Calcium. In terms of the total calcium taken from the soil by the spinach crop, perhaps the outstanding revelation of the study is the fact that the amounts were greatest, and in closest agreement with the calcium increments as soil treatments, in the acid soil. The graph for this soil in figure 2 is almost a straight line from 406.3 mgm. of calcium in the crop with no treatment to 795.5 mgm. where 12 m.e. of calcium was added to the soil. For the neutral soil the relation of calcium increase within the crop to those increments added to the soil is not so consistent. The calcium ranges from 256.9 to 424 mgm. In only one

treatment on the neutral soil was the total calcium of the crop higher than that in the acid soil with no calcium additions. This difference amounted to only 17.7 mgm. or about 4 per cent. In the acid soil the larger calcium application increased the total calcium in the crop by about 96 per cent; in the neutral soil, by 65 per cent. In terms of the total amounts of calcium taken from all the soils by all the 200 plants, that on the neutral soil was 1.671 gm., and that on the acid soil, 3.004 gm. This represents an increase of 1.333 gm. of calcium, or 79 per cent more taken from the same calcium addition to a soil at pH 5.2 than from the same soil at pH 6.8. Rather than producing a detrimental effect, soil acidity provided an increased efficiency—in terms of use by plants—of the calcium supplied in an available, or exchangeable, form on the clay complex of the soil.

These facts are particularly significant when viewed in terms of the differences in concentration of the calcium within the crop. When 3 m.e. of calcium was applied, the spinach grown on the acid soil contained 0.97 per cent of this element, and on the corresponding neutral soil, but 0.60 per cent. When 12 m.e. was applied, the crop concentration of calcium on the acid soil was 0.73 per cent greater than that on the neutral soil. Thus, on the acid soil, the smallest addition of calcium reflected itself as an increase of 60 per cent, and the largest addition as an increase of 110 per cent in the concentration of this nutrient within the crop.

The significance of the increments of calcium within each series was outstanding in the acid soil, but much less so in the neutral soil. The introduction of these increments into the soil did not increase the calcium concentration in the crop as a straight-line function, though it was more nearly so in the acid than in the neutral soil. In the acid soil the concentration rose from 0.92 to 1.39 per cent in the crop, on a dry-weight basis. In the neutral soil the corresponding rise was from 0.53 to 0.66 per cent. The maximum calcium application to the acid soil gave a calcium concentration in the crop more than twice as great as that in the crop with the same calcium treatment on the neutral soil and 2.6 times that of the crop with no treatment on the neutral soil.

In terms of its mobilization into the crop, the addition of calcium was much more efficient on the acid soil than on the neutral soil. Of the total calcium applied throughout the series on the neutral soil, but 1.6 per cent was recovered in the crop. On the acid soil the corresponding efficiency figure was 4.05 per cent. Thus, the efficiency of a calcium application in terms of its recovery in the spinach crop was 2½ times as great on the acid soil as on the neutral soil.

The crop composition and the crop yields reflected the calcium treatments quite differently. The crop was 7 per cent larger, as a mean figure, on the neutral soil than on the acid soil. But in terms of calcium concentrations and calcium totals within the crop these were approximately 250 per cent greater on the acid than on the neutral soils. This indicates a far greater activity of the calcium in the soil, or greater availability to the plant, when a significant amount of hydrogen is present than when a soil is of neutral reaction. It raises the question whether nutrient cation mobility is not increased for plant growth improve-

ment by the presence of hydrogen ions rather than by their complete exclusion from the soil.

Magnesium. There was a close similarity between the total magnesium moved into the spinach crop and the calcium so mobilized, even though the soil additions of magnesium were constant while those of calcium represented increasing amounts. On the acid soil, the total magnesium in the crop increased almost regularly as the soil was given more calcium, as is shown in figure 3. On the neutral soil the total magnesium in the crop for each calcium treatment was higher than that for no calcium addition, but there was no agreement between the magnesium and the calcium amounts, as was suggested by the acid soil. The graphs showing variations in the total magnesium reflects a similarity to the

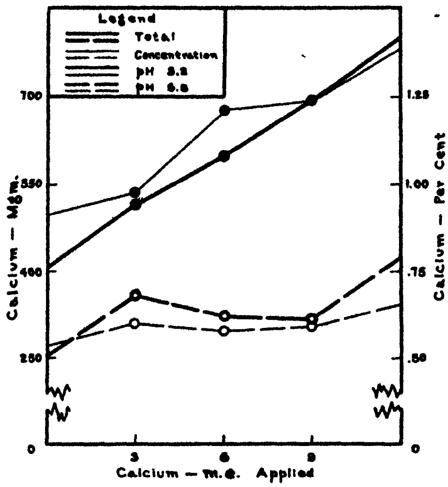

FIG. 2. CALCIUM IN SPINACH IN RELATION TO EXCHANGEABLE CALCIUM APPLIED TO SOIL AT DIFFERENT DEGREES OF ACIDITY

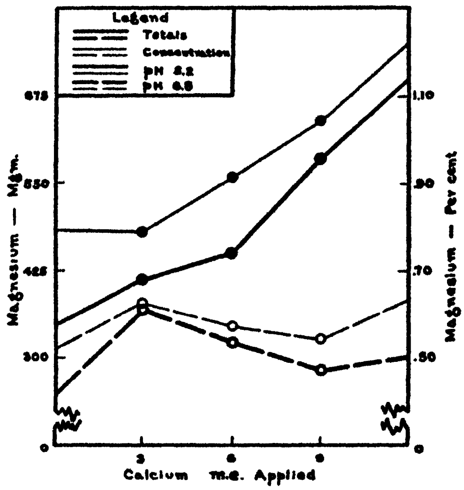

FIG. 3. MAGNESIUM IN SPINACH IN RELATION TO EXCHANGEABLE CALCIUM APPLIED TO SOIL AT DIFFERENT DEGREES OF ACIDITY

graphs for the total calcium in figure 2, but the variations from a straight line are greater. The highest calcium treatment on the neutral soil gave a total magnesium content but 54.1 mgm. higher than that on this soil given no calcium treatment, and lower than that for any of the calcium treatments on the acid soil.

The concentration of magnesium in the crops on the neutral soil was in no case so great as that on the acid soil with no calcium treatment, as is shown in figure 3.

It is significant to note the close similarity in behavior of the magnesium in the crop to that of calcium, despite the fact that variable amounts of calcium were applied to bring about corresponding calcium behavior and that the amounts of magnesium applied were constant. Magnesium, also a divalent ion chemically akin to calcium, seems closely allied with the latter when recovery of the two as totals and concentrations within the crop run so closely parallel. This occurred when in the series of soils the increasing calcium meant increasing calcium saturation but decreasing magnesium saturation.

Strontium. No applications of strontium were made to the soil; nevertheless, both the total and the concentration of strontium in the spinach crop increased as the acid soils carried more exchangeable calcium. On the neutral soil in no case was either the total or the concentration of strontium as high as on the acid soil. The neutral soil, however, delivered slight increases in total and in concentration of strontium with increasing applications of calcium, as is shown in figure 4.

Manganese. Again, with no addition of manganese to the soil, both the total and the concentration of this micronutrient within the spinach crop manifested a behavior similar to that of strontium. On the soil at pH 6.8, however, the increments of calcium in the soil were without effect. On the acid soil, as shown

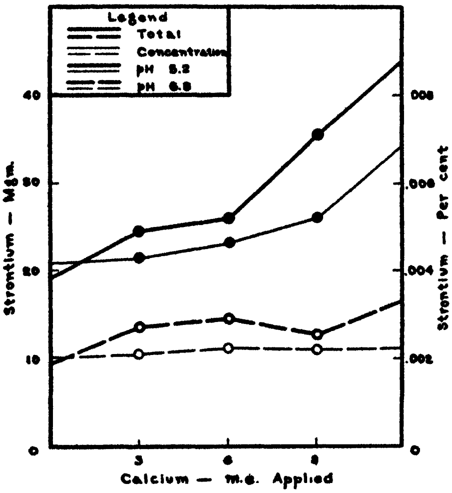

FIG. 4. STRONTIUM IN SPINACH IN RELATION TO EXCHANGEABLE CALCIUM APPLIED TO SOIL AT DIFFERENT DEGREES OF ACIDITY

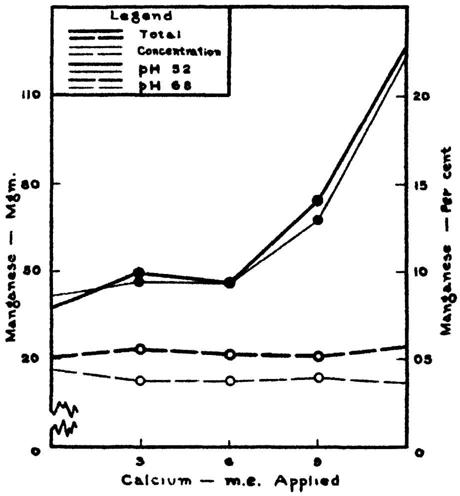

FIG. 5. MANGANESE IN SPINACH IN RELATION TO EXCHANGEABLE CALCIUM APPLIED TO SOIL AT DIFFERENT DEGREES OF ACIDITY

in figure 5, the relative effects by these increments were even more pronounced than for the strontium. The relation between calcium, manganese, and hydrogen (soil reaction) is particularly interesting since it was previously shown (1) that calcium, through its service as a plant nutrient, functions in mobilizing manganese into the crop; this is more pronounced when it does not serve as a reducer of hydrogen concentration. The data for the utilization of manganese by spinach suggest that if calcium is to function in this nutritional role, then the presence of hydrogen along with the calcium is a requisite.

The possible influence of the exchangeable calcium on the total and the concentration of magnesium, strontium, and manganese in the crop deserves particular notation. With increments of calcium, but not of the other three ions, there were increases as totals and as concentrations of the other three, with the exception of manganese in the neutral soil. These influences by the calcium

on the other elements were always far greater in the acid soil. If these are the facts, liming of a soil demands caution lest one apply sufficient carbonate to remove completely the beneficial hydrogen.

Phosphorus. The total amounts of phosphorus taken from the soil by the spinach crop differed but little for the two different degrees of soil acidity. The acid soil gave a slightly higher concentration of the phosphorus in the spinach where 3, 6, and 12 m.e. of calcium were used, but these differences were not relatively large. These two conditions are revealed in figure 6.

It is interesting to note that with constant applications of phosphorus to the soil, the difference in degree of acidity does not give significant difference in the total phosphorus in the crop, as shown by the close proximity of the two curves

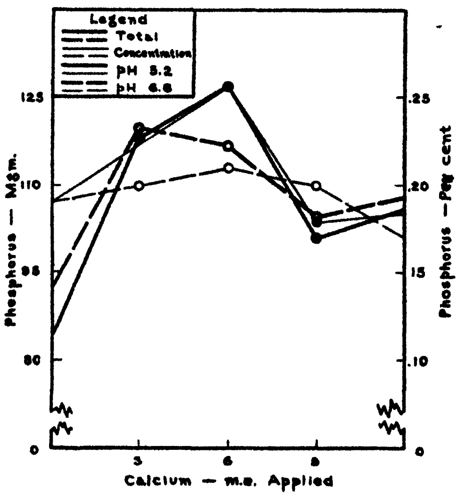

FIG. 6. PHOSPHORUS IN SPINACH IN RELATION TO EXCHANGEABLE CALCIUM APPLIED TO SOIL AT DIFFERENT DEGREES OF ACIDITY

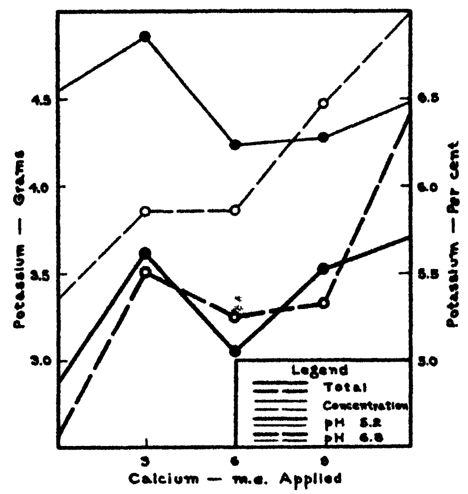

FIG. 7. POTASSIUM IN SPINACH IN RELATION TO EXCHANGEABLE CALCIUM APPLIED TO SOIL AT DIFFERENT DEGREES OF ACIDITY

in the figure. It is significant, however, to note the influence of the variation in exchangeable calcium on the total and on the concentration of phosphorus in the crop. This suggests that the calcium in the soil, rather than the reaction degree, determined the amount of phosphorus that went into the crop. That the increments of 3 and 6 m.e. of calcium should have given more phosphorus in the crop that did 9 and 12 m.e. when the total crop growth of the former two was less than that of the latter two, is an interesting observation. There is a similar situation for the concentration of phosphorus in the crop.

Potassium. The behavior of total potassium in the crop, like that of the phosphorus, depended, not on the degree of acidity in the soil, but on the application of calcium. The concentration of potassium in the crop was influenced markedly by the calcium on the neutral soil, but not on the acid soil, as revealed in figure 7. It is significant that the concentration in the crop was highest on the acid soil when but 3 m.e. of calcium was applied but was not highest on the

neutral soil until 12 m.e. was applied. It may be significant that, as previously mentioned, the concentration of calcium was higher by almost 50 per cent when 3 m.e. was added to the acid soil than when 12 m.e. was applied to the neutral soil. This suggests that on the neutral soil an increasing concentration of calcium in the crop was still possible without disturbing the potassium concentration. But on the acid soil, with its more effective delivery of calcium, there was sufficient increase in concentration within the plants, even at this low calcium offering, to suppress the concentration of potassium, if credence is to be given to the commonly accepted calcium-potassium "antagonism," or probably more properly, the "Kalk-Kali Gesetz" of Ehrenberg. In the interrelationships of the different nutrient cations, both within the soil and within the plant, the nonnutrient cation hydrogen must also be considered, particularly when most biological activities are so commonly associated with acid reactions.

The fact that the quantities of phosphorus and potassium absorbed by spinach are not so nearly straight line functions when related to the calcium increments as was the case for the other elements is an interesting but not a wholly unexpected phenomenon. Davidson (3) pointed out that the "effect of hydrogen-ion concentration on the absorption of phosphorus and potassium is physiological in nature," and that the same causes were operative in the field as in water cultures. As a possible explanation, he pointed to the "iso-electric relations of the ampholytes of the living cell" (2).

In discussing his field results, Davidson (3) points to the possibility of

> . . . a wide range in the iso-electric points of the plant ampholytes, allowing the occurrence of both electro-positive and electro-negative ampholytes within certain limitations of hydrogen ion concentration. This makes possible the simultaneous accumulation of cations and anions. A change in the reaction of the medium may modify, to some extent, the reaction within the plant cells and thus cause a shift of some of the electropositive ampholytes to the negative side and vice versa. This may cause an increased absorption of cations or anions, respectively, which is the explanation offered for the effect of hydrogen ion concentration on the absorption of potassium and phosphorus by wheat plants in the parallel experiments with water cultures and under field conditions.

According to the data of the studies reported herein, the increased hydrogen-ion concentration in the medium brought movement into the plant of larger quantities of the dibasic cations, calcium, magnesium, and strontium, and of the septibasic cation manganese; but for the monobasic cation, potassium, and for the anion phosphorus, the hydrogen-ion concentration of the medium was without such effect. There is a decided physiological significance, however, in the fact that the behaviors of the potassium and the phosphorus, one a cation and the other an anion, suggest a precipitation-peptization curve for colloids like protein and at each of the two different degrees of acidity. They do not indicate acidity neutralizations. Rather, they suggest calcium as a factor in modifying the physiology of the plant which in its behavior like an ampholyte gives minima for phosphorus at 0 and 9 m.e. of calcium, and maxima at 3–6 and 12 m.e. For potassium utilization, the minima were at 0 and 6 m.e. and the maxima at 3 and 12 m.e. of calcium provided by the media in both the acid and

neutral reactions. For both phosphorus and potassium, then, there were two minima and two maxima, for the total and for the concentration whether at pH 5.2 or 6.8, save for the concentration of phosphorus at the latter pH figure.

These performances by the phosphorus and the potassium, both of which were disturbed but little by the hydrogen-ion differences but followed a curve suggesting ampholytic behavior as induced by the calcium increments, give emphasis in this study to the physiological behaviors of all the ions more than to simple neutralizations and common reaction differences. The influence by the hydrogen ion in "mobilizing" more of the dibasic cations into the plant might, at first thought, be viewed simply in the light of the neutralization concept. But when the hydrogen concentration difference is without effect on the behavior of potassium—a similar but more active monobasic cation—and on the behavior of phosphorus—an anion—and when both of these apparently follow the suggested effects by calcium on an ampholyte, then the behavior of all the ions considered moves into the physiological sphere of the plant rather than remaining in the simple acidity concept.

Disease and nutrition

That the role of the hydrogen ion in its inimical effects on potato scab may be exercised physiologically through its influence on the other nutrient cations, is suggested by the observations of the scabbiness of the potatoes in this experiment. The amount of scab increased with increments of exchangeable potassium in the soil over the constant level of calcium, and also with increments of exchangeable calcium over the constant level of potassium at the three different soil reactions, viz., pH 5.2, 5.5, and 6.8. It is significant that either of these distortions of the nutrient levels reflected itself as a metabolic disturbance in the plant by increase in scabbiness far more severely on the neutral than on the acid soil. Even though this suggests that the infestation by the potato scab organism is more a matter of proper plant nutrition than merely of soil reaction, it points to the hydrogen as an agency in making for better nutrition. If hydrogen plays this apparent role of mobilizing the exchangeable nutrients in the soil irrespective of their levels, it suggests that hydrogen may be contributing a service in guaranteeing the large variety of nutrients requisite for plant growth. It suggests that it may be fulfilling in a large measure the condition suggested by True (9) when he says, "The larger the variety of ions present the greater may be the absorption of all the electrolytes and the less marked the importance of the proportional concentration between ions."

SUMMARY

Studies with spinach and potatoes at constant and controlled levels of exchangeable nutrients in the soil but at different degrees of acidity have shown far greater mobilization of the nutrients into the crop when the soil was acid than when it was neutral. In some cases this reflected itself as increased crop yields, but in all cases of the chemical analyses it was evident in the form of increased concentration of many of the different elements in the plant tissue. The results

point forcefully to the possible role by the hydrogen ion in bringing about a greater availability of the exchangeable nutrients in the soil so that the presence of this ion may be serving as a benefit rather than as a detriment.

Of the possible cations taken by plants, calcium, magnesium, strontium, and manganese were moved into the spinach crop in greater amounts and greater concentrations in the presence of significant hydrogen concentration than in the soil that was nearly neutral. The only other nutrient ions considered in the study, potassium and phosphorus, manifested a different behavior. Though their utilization by the crop was not widely different according to the presence or absence of hydrogen ions, yet both the totals and the concentrations suggested a precipitation-peptization behavior according to the amounts of exchangeable calcium in the soil.

All of these facts serve to emphasize the significance of hydrogen and calcium in the soil to plant physiology much more than as opposing forces in determining soil reaction.

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APPLICABILITY OF THE MITSCHERLICH METHOD TO THE DETERMINATION OF AVAILABLE PHOSPHATE IN SOME IOWA SOILS[1]

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In the upper horizons of many Iowa soils the supply of available phosphate, as measured by chemical extraction methods, is relatively low, yet significant crop responses to the application of phosphate fertilizers are not invariably obtained. Those biological methods of assessing availability of soil phosphate which depend on plant growth might be expected to give more reliable information as to the available phosphate level than chemical extraction methods. Perhaps the best known plant method is that developed by Mitscherlich and used extensively in East Prussia for the routine testing of soils. The method has a clearly defined theoretical basis developed from a knowledge of the relationship between yield increases and increments of any limiting growth factor. The validity of the logarithmic equation expressing this relationship has been questioned by a number of workers. Criticisms have also been directed against the assumed constancy of the "effect" factors for the various nutrients and the arbitrary choice of conversion factors for interpreting pot results in terms of field values. Much of the extensive literature on this subject has been reviewed by Stewart (9), and more recently by De Vries (11, 12).

The great volume of papers of controversial character has perhaps obscured the fact that, as carried out by Mitscherlich, this method has apparently proved successful in the prediction of the fertilizer need of soils. Outside of northern Europe, however, few studies of the practical applicability of the method have been reported. Capó (2) investigated the reliability of the method for determining the available nutrients in some Puerto Rican soils, and preferred to use the special equation for the determination of the initial nutrient content of single nutrients rather than the general equation relating yield to the amounts of the three principal nutrients in the soil. A similar study was made on seven Hawaiian soils by Magistad (3). Duplicate soil samples were sent to Königsberg to be tested by Mitscherlich. The same variety of oats was employed by both workers, and identical increments of the various nutrient elements were added. The apparent amounts of available nutrients, when determined under Hawaiian conditions, were much greater than those found by Mitscherlich in Germany.

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[2] Formerly research assistant, now associate agronomist, Mississippi State College, and research professor of soils, respectively. Thanks are due F. B. Smith, now professor of soils at the University of Florida, for his help during the initial stages of these studies; D. L. Holl for advice in the mathematical treatment of the data; and A. J. Englehorn for greenhouse data on certain of the soils.

The discrepancy was greatest in the case of available phosphorus. The differences no doubt had their origin in the inconstancy of the effect factor, the magnitude of which was probably affected by the longer growing period before maturity in Hawaii and by the higher mean temperature. These comparative studies suggest the importance of the choice of an indicator plant properly adapted to local climatic conditions. The assumption was apparently made that the effect factor for each nutrient is independent of environment and season of the year.

Smith, Brown, and Neal (8) studied the fertilizer needs of Carrington loam by various methods, including tumbler and pot tests modeled on, but not identical with, the Mitscherlich procedure, and obtained a yield curve for superphosphate applications that fell close to the curve of yields calculated from the Mitscherlich equation.

The general purpose of the experiments described in the present paper was to test the suitability of the Mitscherlich method for the determination of available phosphorus in some Iowa soils. This involved, first, the investigation of the magnitude of the "effect" factor *c* for phosphorus under Iowa conditions, since doubts have been expressed as to the general applicability of the figure given by Mitscherlich, and second, the constancy of the effect factor at different seasons of the year and with different varieties of oats.

MATERIALS AND METHODS

Five experiments were carried out, 30 standard Mitscherlich pots[3] being used in each. The management technique, as given by Mitscherlich (4), was followed closely. Each pot contained 2 kilos of air-dry soil mixed with 4.67 kilos of pure crystal silica sand. The basal treatments applied to all pots were: 1.5 gm. K_2O in the form of K_2SO_4, 1.1 gm. N in the form of NH_4NO_3, 1.5 gm. $CaCO_3$, and 0.5 gm. NaCl. The maximum amount of phosphorus added was 1.0 gm. P_2O_5 per pot, in the form of a filtered extract of 20 per cent superphosphate as prescribed by Mitscherlich. All treatments were replicated three or more times. The moisture content was closely controlled by weighing daily and, when necessary, twice daily throughout the experiment.

Details of the five experiments are given in table 1. The oats variety in experiments I–IV was a new Victoria-Richland cross. A related but not identical cross of greater rust resistance was used in experiment V. One soil, Clarion loam, was included in all experiments. This was obtained from the south border of plots 811 and 816 in the 2-year corn-oats rotation at the Agronomy Farm, Ames. These plots have received no applications of phosphate for 25 years. Fair responses have been obtained to additions of phosphate with manure on adjoining plots in the same block.

RESULTS

Determination of the effect factor c

The average yields in grams per pot for each of the yield curve experiments, set up for the purpose of determining the magnitude of the phosphate effect factor *c*, are given in table 2. The treatments were replicated four times in ex-

[3] Purchased from Gebrüder Bauman, Stanz and Emaillierwerke, Amberg-Opf., Germany.

TABLE 1

Description of experiments

EXPERIMENT	SOIL	pH	GROWING PERIOD	LOCATION	PURPOSE
I	Clarion (Agron. Farm), April 1938	5.7	April 18 July 11, 1938	Outdoors*	Determination of effect factor c
II	Clarion (Agron. Farm), July 1938	5.7	July 20 October 21, 1938	Outdoors*	Determination of available phosphorus
	Carrington (Marion)	5.7			
	Tama (Greenfield)	5.6			
	Marshall (Cherokee)	5.5			
	Grundy (Melcher)	5.7			
III	Clarion (Agron. Farm), October 1938	5.7	October 22 February 13, 1938 39	Greenhouse	Determination of effect factor c
IV	Clarion (Agron. Farm), October 1938	5.7	February 14 May 19, 1939	Greenhouse	Determination of available phosphorus
	Clarion (Woodward), 1938	5.2			
	Clinton (Lockeridge)	5.3			
	Fayette (Waukon)	5.5			
	Marshall (Shenandoah)	5.2			
V	Clarion (Agron. Farm), March 1940	5.7	April 4- June 12, 1940	Greenhouse	Determination of available phosphorus and effect factor c
	Clarion (Woodward), 1939	5.2			

* Oats grown in outdoor wire cage, sheltered from direct rainfall.

TABLE 2

Yields of oats as affected by varying applications of phosphate

Experiments I and III

P_2O_5 APPLIED PER POT	AVERAGE YIELD (OVEN-DRY) PER POT					
	Outdoors—Exp. I*			Greenhouse—Exp. III		
	Grain	Straw	Total	Grain	Straw	Total
gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
0.000	5.5	10.6	16.0	2.1	12.3	14.4
0.077	8.6	15.0	23.6	3.7	18.1	21.8
0.192	12.6	23.1	35.7	5.6	30.6	36.2
0.383	15.3	24.3	39.7	7.2	44.5	51.7
0.613	17.7	28.8	46.6	6.2	49.6	55.8
1.000	15.5	33.3	48.8	6.8	53.2	60.0

* Standard error for experiment I = ± 0.58 gm. per pot.

periment I and five times in experiment III. The plants at 1 month and at maturity are illustrated in figure 1.

The yield curves plotted from these data are given in figures 2 and 3.

The effect factor c defines the slope of the straight line obtained if the Mitscherlich equation is written in the following form

$$\log \frac{A - y}{A} = -c(x + b)$$

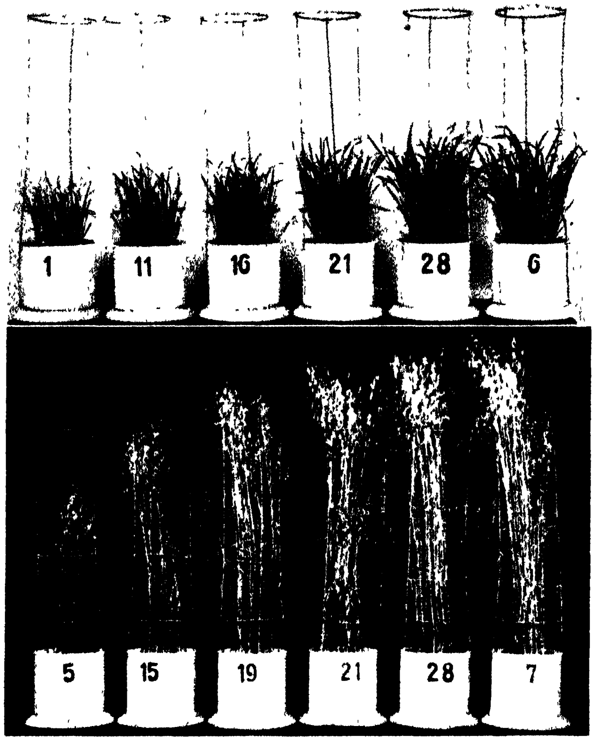

FIG. 1. GROWTH OF OATS ON CLARION LOAM IN MITSCHERLICH POTS
Mitscherlich experiment I: top, growth at 1 month; bottom, growth at maturity

POT NUMBERS	P_2O_5 APPLIED	AVERAGE HEIGHT	
		One month	Maturity
	gm.	*cm.*	*cm.*
1, 5	0.000	25	52
11, 15	0 077	32	66
16, 19	0.192	35	80
21	0 383	40	84
28	0 613	42	90
6, 7	1 000	41	93

in which A is the maximum yield per pot in grams; x, the quantity of nutrient applied, in this case phosphate; y, the yield produced by the application of x; and b, the amount of that nutrient initially present in the soil. Had equal increments of phosphate been employed in the determination of the

yield curves, assuming that the curves were logarithmic, the proper value of A to substitute in this equation could have been determined by calculation. Since equal increments of phosphate were not applied, some selection had to be made. Three possibilities offered themselves: first, the use of the highest individual pot yield; second, the use of the mean of the yields of the replicates receiving the highest phosphate application; third, the use of a value determined by trial to give a logarithmic curve best fitting the experimental yields, as indicated by the r value. The third was selected, and the inserts in figures 2 and 3 show the position of the experimental points in relation to the straight lines derived from them according to the method of least squares.

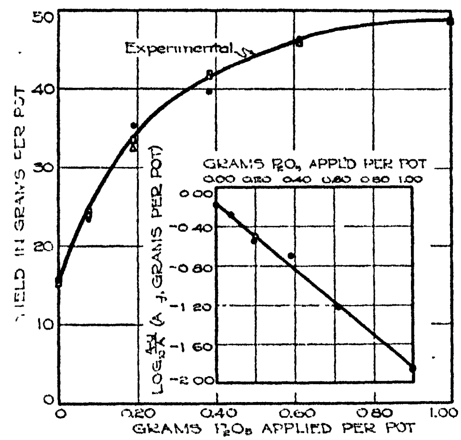

FIG. 2

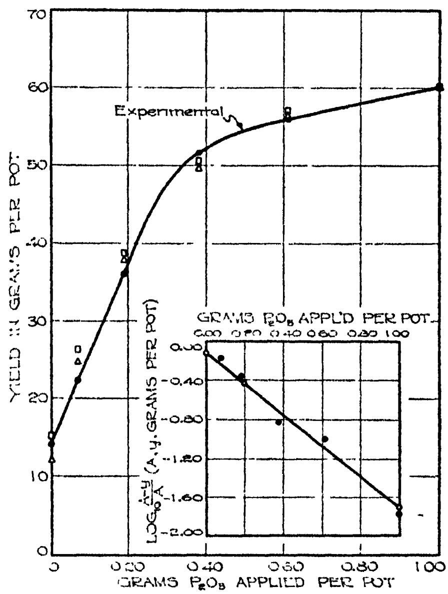

FIG. 3

FIG. 2. YIELD DATA FROM MITSCHERLICH EXPERIMENT I
Experimental data ●; calculated yields, b_1 values □, b_2 values △

FIG. 3. YIELD DATA FROM MITSCHERLICH EXPERIMENT III
Experimental data ●; calculated yields, b_1 values □, b_2 values △

The equations of the lines to determine c were

Experiment I	$E = -0.1627 - 1.6825x$ ($A = 49.5$; $r = -0.996$)
Experiment III	$E = -0.0947 - 1.6797x$ ($A = 61.0$; $r = -0.997$)

Since E (estimated value, y axis) $= \log \frac{A - y}{A}$, c can be taken directly from these equations. The phosphate effect factor c for experiment I was, therefore, 1.682 and for experiment III, 1.680. These values are appreciably lower than the Mitscherlich value, which is 1.95.

Determination of the available phosphate content of soils

A value for the initial nutrient content, b, of the soils is obtained by Mitscherlich by substituting the experimentally determined value for y_0 (the yield when no addition of the nutrient is made) in the following equation.

$$b = \frac{\log A - \log (A - y_0)}{c}$$

In experiments I and III two values for b were obtained; b_1 by using the experimentally determined value for y_0, and b_2 by using the extrapolated value derived from the straight lines given in the inserts of figures 2 and 3. Each of these values was substituted in the equation $y = A(1 - 10)^{-c(x+b)}$, which is another form of the Mitscherlich equation, to determine which gave a curve having the least deviation from the experimental one. Comparisons of the experimental yields with the two sets of calculated yields are shown in table 3, and the values obtained for the latter plotted as points in figures 2 and 3. The value b represents

TABLE 3

Calculated and experimental values of y

Experiments I and III

P_2O_5 APPLIED PER POT	EXPERIMENT I			EXPERIMENT III		
	Experimental	Calculated		Experimental	Calculated	
		$b_1 = 0.1009$	$b_2 = 0.0969$		$b_1 = 0.0696$	$b_2 = 0.0574$
gm.						
0.000	16.0	16.0	15.5	14.4	14.4	12.0
0.077	23.6	24.6	24.2	21.8	26.4	24 7
0.191	35.7	33.6	33.2	36.2	38.8	37.7
0.383	39.7	41.9	41.8	51.7	50.4	49.9
0.613	46.6	46.4	46.3	55.8	56.6	56.4
1.000	48.8	48.8	48.8	60.0	60.0	60.0

the distance from the origin along the x axis to the point at which the yield curve if continued would intersect it. In experiment I the curve giving the value b_1 has slightly less deviation from the experimental than does the one giving the b_2 value, whereas in experiment III the reverse is the case. The most probable values for b would therefore be 0.10 gm. and 0.057 gm. P_2O_5 per pot respectively, which would be equivalent to 44.1 and 25.1 pounds P per surface acre of 2 million pounds. Mitscherlich ordinarily employs the experimental value of y_0 in the calculation of b. If this were followed and the b_1 values accepted in both experiments, the available P content would be equivalent to 44.1 and 30.4 pounds per acre respectively.

Values of b were obtained for nine soils in experiments II and IV, a sample of Clarion loam from the same area as sampled for experiments I and III, being included in both. Average pot yields are given in table 4. In arriving at a value for b in these soils the phosphate effect factor c was taken as 1.68 as determined in experiments I and III. The validity of this step is perhaps questionable until it be proved that c is constant at all seasons of the year for any one

variety. The *b* values for the nine soils, expressed on a field basis, are given in table 5, along with results obtained by the chemical availability methods of Truog (10), Bray (1), and Morgan (6). The response of eight of these soils to

TABLE 4

Yields of oats in experiments to determine available phosphate content of soils

SOIL TYPE AND LOCATION	P_2O_5 APPLIED PER POT	AVERAGE (OVEN-DRY) YIELD PER POT		
		Grain	Straw	Total
	gm.	*gm.*	*gm.*	*gm.*
Experiment II				
Carrington silt loam	0.0	1.3	6.0	7.3
Marion, Iowa	1.0	2.9	25.7	28.6
Tama silt loam	0.0	2.1	9 4	11.5
Greenfield, Iowa	1.0	3.8	28.3	32.1
Marshall silt loam	0.0	1.5	8.9	10.4
Cherokee, Iowa	1.0	3.8	30.6	34.4
Grundy silt loam	0.0	2.8	10.1	12.9
Melcher, Iowa	1 0	3.7	31.9	35.6
Clarion loam fertility plots 811, 816				
Agronomy Farm	0.0	1.5	7.1	8.6
Ames, Iowa	1.0	4.6	31.2	35.8
Experiment IV				
Clarion loam	0.0	6.1	13.6	19.7
Woodward, Iowa	1.0	13.4	65.2	78.6
Clinton silt loam	0 0	4 9	13.6	18.5
Lockeridge, Iowa	1.0	11.8	62.8	74.6
Fayette silt loam	0 0	5.9	17.7	23.6
Waukon, Iowa	1.0	12.2	63.1	75.3
Marshall silt loam	0.0	6 3	17.2	23.5
Shenandoah, Iowa	1.0	12.9	71.8	84.7
Clarion loam fertility plots 811, 816				
Agronomy Farm	0.0	2.6	9.9	12.5
Ames, Iowa	1.0	8.5	63.4	71.9

the addition of the equivalent of 400 pounds of superphosphate per acre when successively cropped to sudan grass and wheat in the greenhouse are also included.[4]

[4] These experiments were carried out by A. J. Englehorn as part of a larger investigation, full details of which will be published elsewhere.

Concurrent determination of the effect factor c *and the available nutrient content* b

Since there was no certainty that the effect factor for phosphate is a constant if environmental and climatic conditions are changed, an experiment was set up in such a way that the determination of *c* and the calculation of *b* would be possible from the same data. This modification involved the addition of three equal increments of phosphorus and called for the use of 12 pots for the testing of one soil

TABLE 5

Comparison of available phosphorus determinations by the Mitscherlich method with results obtained from chemical tests and greenhouse experiments

SOIL TYPE	MITSCHERLICH	TRUOG	BRAY	MORGAN	GREENHOUSE RESPONSE TO EQUIVALENT OF 400 POUNDS SUPERPHOSPHATE PER ACRE
	lb./A.	*lb./A.*			
Carrington silt loam	33	12	v. low	v. low	Sudan** Wheat*
Tama silt loam	50	34	low	v. low	Sudan⁰ Wheat⁰
Grundy silt loam	51	50	medium	low to v. low	Sudan⁰ Wheat*
Marshall silt loam (Cherokee)	41	26	low	v. low	Sudan* Wheat**
Clarion loam (Woodward)	33	46	low	v. low	Sudan* Wheat**
Clinton silt loam	32	32	low	v. low	Sudan⁰ Wheat⁰
Fayette silt loam	43	40	medium	v. low	Sudan⁰ Wheat⁰
Marshall silt loam (Shenandoah)	37	64	medium	low to v. low	Sudan⁰ Wheat⁰
Clarion loam (Agronomy Farm)					
Exp. I.	44	42	low	v. low	......
Exp. II	31				
Exp. III	25				
Exp. IV	22				
Exp. V	18				

⁰ Not significant.
* Significant.
** Highly significant.

in place of the six recommended by Mitscherlich. The obvious amounts of phosphate to add would be equivalent to 0, 0.33, 0.66, and 1.0 gm. P_2O_5 per pot. Inspection of earlier experimental curves showed, however, that unless the soil was markedly deficient in available phosphorus, the yields from the intermediate applications might so nearly approach the maximum that the curve would not be well delineated. Accordingly, six additional pots were included with applications of 0.2 and 0.5 gm. per pot, giving in effect two series, 0, 0.2, 0.5, and 1.0 gm. per

pot and 0, 0.33, 0.66, and 1.0 gm. per pot. The soil employed was Clarion loam from Woodward. In a parallel experiment, the Clarion loam from the Agronomy Farm, freshly sampled, was again included, in this case the lower series of phosphate applications only being made. The yields in grams per pot are given in table 6. The results from both soils differed considerably from those obtained in Mitscherlich experiment IV in that the grain yields were higher and the straw yields appreciably lower at maturity in experiment V, in part no doubt because of a varietal difference of the oats, and in part perhaps because of environmental differences.

Similarly the response to phosphorus given by the Agronomy Farm Clarion loam in this experiment was distinctly different from that obtained in experiments I and III.

Statistically significant increases in yield on Clarion loam (Woodward) were not obtained from applications of phosphate in excess of 0.5 gm. P_2O_5 per pot, and accordingly the two series of applications were considered together as one experiment, in order to have more than one point on the curve below the maximum.

TABLE 6

Yields of oats as affected by varying applications of phosphate

Experiment V

P_2O_5 APPLIED PER POT	AVERAGE (OVEN-DRY) YIELD PER POT					
	Clarion (Woodward)			Clarion (Agronomy Farm)		
	Grain	Straw	Total	Grain	Straw	Total
gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*
0.00	7 7	11.8	19 5	5.5	11.9	17.4
0.20	20.5	35.4	55.9	16.4	42.2	58.6
0.33	20.8	38.7	59.5	...	...	..
0.50	22.0	40.4	62.4	18.3	44.6	62.9
0.66	20.8	40.3	61.1	.	..	..
1.00	20 8	40.9	61 7	18 8	44.7	63.5

The yield data from both soils conformed reasonably well with logarithmic curves of the Mitscherlich type. The equations of the lines determining c were:

Clarion loam (Woodward) $E = -0.1741 - 3.5116x$ $(r = -0.997)$
Clarion loam (Agronomy Farm) $E = -0.2387 - 3.455x$ $(r = -0.986)$

and the values of c, therefore, were 3.51 and 3.45 respectively. The available phosphorus present in these soils was then ascertained by using the figures for c determined in this experiment, and applying the necessary "dilution" factor as outlined by Mitscherlich. The amounts indicated were 20.0 and 17.5 pounds P per surface acre respectively.

GENERAL DISCUSSION

Agreement of yield curves with Mitscherlich form

The requirements of the Mitscherlich procedure are fully met if the arithmetic means of the combined grain-straw yields in three replicate pots are taken as the

yield data. Though this may be satisfactory in simple tests in which *b*, the amount of available nutrient present, is the only point at issue, and in which basal and maximum yields only are determined, it is less convincing when the experiment is conducted for the purpose of determining the effect factor *c*, in which case the yield curve must be satisfactorily delineated, not assumed. The significance of small differences in the yield means produced by increasing increments of the nutrient is not considered but may, in fact, vitally affect the question as to whether or not the response curve, as experimentally determined, is a good fit to a logarithmic curve. This is particularly true of the yield data for Clarion loam (Agronomy Farm) in experiment V. In this case the differences in yield produced by additions of 0.2, 0.5, and 1.0 gm. P_2O_5 are not statistically significant, although the means show a progressive yield increase. In these experiments the arithmetic means only have been employed and the fair agreement of all the yield curves (experiments I, III, and V) with theoretical curves of the Mitscherlich form seems to indicate that the Mitscherlich equation properly expresses the relationship between the yield and the initial concentration of a single nutrient in the soil, though it could not be said to prove it in a rigid mathematical sense.

Constancy of c

The values of *c* obtained when the same variety of oats was grown outdoors and in the greenhouse at different seasons of the year were in good agreement, being appreciably lower than the Mitscherlich value of 1.95 (presumably for Lockows Petkuser Gelbhafer oats), and only about one half those derived from experiment V when a closely related but different variety of oats was grown in the greenhouse. Clearly the variety of oats affects the magnitude of the effect factor. What has not yet been established unequivocably, and what would have to be ascertained if it were proposed to set up a testing system, is whether the *c* value for a selected variety is constant or reasonably nearly constant at different seasons of the year, at different fertility levels, and under different environmental conditions. The efficacy of a testing system would be much reduced if it were possible to use the test plant at only one season of the year. More controversy has perhaps been centered on this question of the constancy of the effect factor than any other phase of the Mitscherlich procedure. The weight of evidence seems to be overwhelmingly against absolute constancy, and this has been partly admitted by Mitscherlich (5).

Available phosphate content of soils, b

In arriving at a value of *b* for the nine soils tested in experiments II and IV, the constancy of *c* for that variety of oats was assumed. There was some measure of agreement between the ranking of these soils on the basis of the Mitscherlich test and that given by the Truog and Bray chemical availability methods for the determination of available phosphorus. Further there was, as might be expected, reasonable agreement between the results of the Mitscherlich test and the responses made by successive crops of sudan grass and wheat to the addition of 400 pounds superphosphate per acre to the undiluted soil in the greenhouse.

Significant response by both crops was obtained only on soils ranked low according to the *b* values, though not all those with low *b* values gave significant responses.

Five values in all were obtained for Clarion loam from the Agronomy Farm sampled from the same site at four different times. Only three of the figures were arrived at from experiments which concurrently provided information about the magnitude of *c*. Although it would not be expected that the available phosphate content of this soil would be unvarying, the extent of the variation is disturbing. In spite of the great differences in the *c* factors for the varieties of oats employed, the two Clarion samples included in experiments IV and V were ranked similarly, but their relative difference in phosphate content was not the same.

Possible modifications in procedure

If the Mitscherlich method were to be applied in practice in testing Iowa soils for available phosphate, it would be necessary, first, to establish the effect factor for the selected variety of oats employed, and secondly, to investigate the constancy of that factor. This would involve extensive experimentation. As an alternative, however, the procedure might be so modified that the data necessary for calculating the effect factor *c* would be provided by each test, so that all doubt as to the proper value to be employed in deriving *b* would be removed. The concurrent determination of *c* and *b* could be accomplished by making three equal increments of phosphate of 0.1, 0.2, and 0.3 gm. P_2O_5 per pot in triplicate, in this way satisfactorily delineating the lower part of the yield curve. This modification would require the use of 12 pots for testing one soil instead of 6, as used by Mitscherlich when the constancy of *c* is assured. The maximum yield *A* could be calculated by assuming a logarithmic response curve, or if desired could be determined experimentally by the addition of 3 extra pots each receiving 1.0 gm. P_2O_5.

A further possibility would be to make use of the methods of calculation suggested by Rauterberg (7) which permit the determination of *A* and thence of *b* without of necessity calculating the effect factor *c*. The number of pots involved would be the same, but the increments added would have to be in a geometrical series of 2, that is, y_0, y_1, y_2, y_3 would receive respectively 0, 0.1, 0.2, and 0.4 gm. P_2O_5.

It would also be highly desirable to find an indicator plant that would mature more rapidly than oats, or to obtain yield data at a stage earlier than maturity, in order to shorten the time required (nearly 3 months) to test a soil for its fertilizer needs by the Mitscherlich method. Capó (2) used sorghum in place of oats as the indicator crop in Puerto Rico, and Mitscherlich (4) himself suggested the use of millet or rice for tropical conditions. Sudan grass and mustard, harvested before flowering, are at present under investigation in this connection.

SUMMARY

A study was made of the applicability of the Mitscherlich procedure to the determination of the available phosphate in soil under Iowa conditions.

Experimentally determined yield curves for oats, obtained by plotting the mean yields of replicate pots treated with successive increments of phosphate, gave reasonable agreement with logarithmic curves as expressed by the Mitscherlich equation. Not in every case, however, were the increases in yield produced by successive increments statistically significant.

The phosphorus effect factor, *c*, was distinctly lower for Victoria-Richland oats than the constant used by Mitscherlich. Another variety, closely related, gave a value almost twice as great.

There was some measure of agreement between the ranking of nine Iowa soils in level of available phosphate as tested by the Mitscherlich procedure with rankings obtained by the chemical availability tests of Truog and Bray. Close agreement was found between the results of the Mitscherlich tests on these soils and the responses on the undiluted soils given by successive crops of sudan grass and wheat in the greenhouse after application of the equivalent of 400 pounds of superphosphate per acre.

To be of practical value under Iowa conditions, the Mitscherlich method would desirably be modified in such a way that the effect factor would be determinable separately in each test. This modification would call for the use of a minimum of 12 pots for each soil instead of 6, and the use of three small increments of phosphate to delineate satisfactorily the lower part of the yield curve, or alternatively, increments each double its predecessor.

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EFFECTS OF ALUMINUM ON COPPER TOXICITY, AS REVEALED BY SOLUTION-CULTURE AND SPECTROGRAPHIC STUDIES OF CITRUS[1]

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A number of investigators have found that aluminum in small amounts exerts a stimulating effect on plant growth. Most of these workers, including Mazé (6), Lipman (5), Scharrer and Schropp (7), and Sommer (8), used such plants as maize, peas, oats, and sunflowers and reported a slight increase in dry weight of the plants with a definite increase in seed production. In work with citrus cuttings, Haas (3) reported a stimulating effect on root growth. It is not certain from any of these studies whether the growth responses noted were due to the indispensability of this element or to some indirect action.

In connection with our work on the nutrition of citrus, some interesting results have been obtained with aluminum. Though it has not been possible thus far to prove whether aluminum is indispensable for the growth of citrus, it has been clearly shown that a small amount of this element is capable of decreasing markedly the toxicity of copper in solution cultures and thereby of causing an increase in plant growth. Spectrographic analyses of the ash of the culture plants have given data on the seat of the aluminum-copper antagonism, as well as interesting information concerning the kinds, amounts, and distribution of micronutrients in the plants grown in purified culture solutions. It is the purpose of this paper to describe the results of this study.

EXPERIMENTS WITH CITRUS PLANTS IN SOLUTION CULTURES

Two experiments were conducted with citrus plants in solution cultures. In the first, Valencia orange cuttings were used; in the second, lemon cuttings.

In both experiments the citrus cuttings were rooted in sand in a propagating bed. Plants as nearly uniform as possible were then selected and transferred to solution cultures in 7.5-liter Pyrex battery jars. These jars were provided with bakelite tops and with painted wood-plug inserts for holding the plants. Pyrex glass aerators were employed in both experiments.

Growth of orange cuttings

The 12 culture plants of this experiment were grown alternately (a) in complete solutions containing all known necessary plant food elements and (b) in solutions complete save for the omission of phosphate. Of the 12 cultures

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lacking phosphate, 4 received aluminum at a rate of 0.5 p.p.m., 4 received aluminum at a rate of 5 p.p.m., and the remaining 4 received no aluminum.

The composition of the complete solution (a), expressed in milliequivalents per liter, was as follows: calcium, 6.28; magnesium, 3.76; potassium, 2.79; sodium, 0.2; chloride, 0.2; nitrate, 10.01; phosphate, 0.33; sulfate, 2.49. Zinc, manganese, and boron were added at the rate of 2 p.p.m. Copper was added at the rate of 0.1 p.p.m. Purified iron sulfate (1), at a rate of 0.2 p.p.m. iron, was added several times a week.

The plants were alternated weekly between the solutions containing phosphate and the solutions containing no phosphate, with and without aluminum. All cultures were continuously aerated, and the pH was maintained between 4.5 and 5.0 by the addition of H_2SO_4 or KOH as required. The experiment was carried on from January 7 to November 1, 1938.

The plants in the cultures receiving no aluminum made very poor growth, the roots gradually taking on a brownish, unhealthy appearance, with some stubbiness of laterals, and the leaves becoming lusterless and rather bronzed in appearance. In the cultures receiving 0.5 and 5 p.p.m. aluminum, however, root growth was much more vigorous, and the tops were green and made good growth. Pictures of top and root growth of representative plants in the aluminum and no-aluminum cultures are shown in figures 1 and 2.

The similarity between roots in the no-aluminum cultures and roots injured by excess copper suggested that perhaps the poor growth in these cultures was due to the presence of too much copper and that the stimulating effect of the aluminum was no more than the reflection of its antagonistic effect on the copper.

FIG. 1. TOP GROWTH OF 10-MONTH-OLD VALENCIA ORANGE CUTTINGS IN SOLUTION CULTURES WITH AND WITHOUT ALUMINUM

A, base nutrient solution only; B, base nutrient plus 0.5 p.p.m. aluminum; C, base nutrient plus 5 p.p.m. aluminum.

FIG. 2. ROOT GROWTH OF PLANTS A AND B IN FIGURE 1

FIG. 3. EFFECT OF COPPER AND ALUMINUM ON TOP AND ROOT GROWTH OF 5-MONTH-OLD LEMON CUTTINGS IN SOLUTION CULTURES

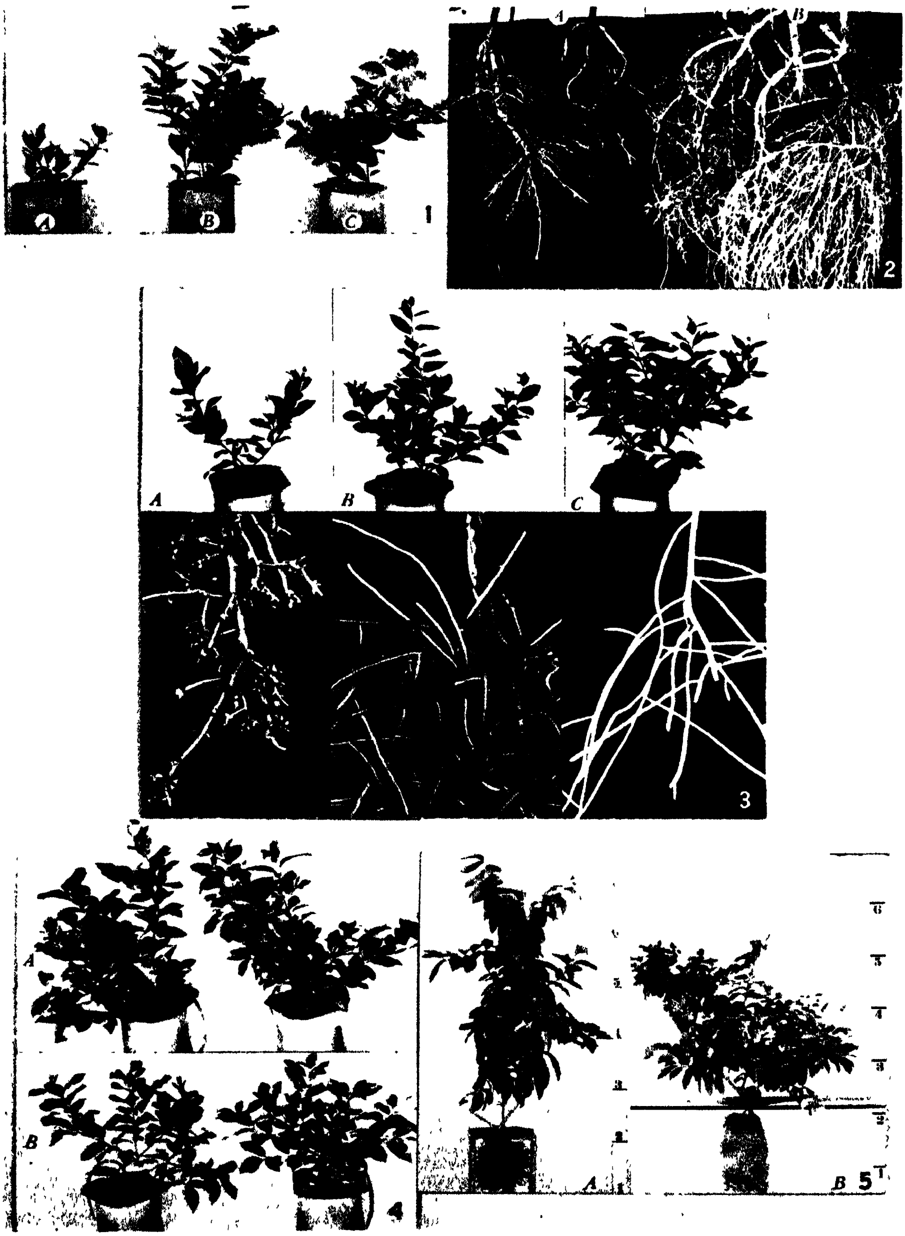
A, Toxic effect of 0.1 p.p.m. copper on growth of plant in culture 14; B, recovery of plant after omission of copper from solution for 1 month (culture 13); C, detoxifying effect of aluminum when added to solution in which copper was present (culture 17). Photographed June 20, 1939; root sections very slightly magnified.

FIG. 4. EFFECT OF ALUMINUM ON TOP GROWTH OF LEMON CUTTINGS

These plants were grown in base nutrient solution plus 0.1 p.p.m., each, manganese, zinc, and boron and 0.05 p.p.m. molybdenum (A) without aluminum and (B) with 0.1 p.p.m. aluminum added. Photographed June 20, 1939, when plants were 5 months old.

FIG. 5. EFFECT OF ALUMINUM ON ROOT AND TOP DEVELOPMENT OF LEMON CUTTINGS

These plants were grown in similar base nutrient solutions (A) plus 0.5 p.p.m. and (B) plus 5 p.p.m. aluminum. Note the greater root development and somewhat depressed top growth in B, in comparison with the more normal growth in A.



FIGS. 1–5

In order to investigate this possibility, a second experiment was set up, employing lemon cuttings.

Growth of lemon cuttings

In this experiment several modifications were introduced. A large volume of base-nutrient solution containing the major elements (that is, calcium, magnesium, potassium, nitrate, sulfate, and phosphate) in approximately the same concentrations as those employed in experiment 1, was purified in a 140-liter tile container by addition of enough $Ca(OH)_2$ to bring about a phosphate precipitation. After the precipitate had settled, the supernatant liquid was siphoned off into 7.5-liter Pyrex battery jars. The reaction was then adjusted with redistilled HNO_3 to pH 4.5, and enough KH_2PO_4 was added to give a concentration of 3 p.p.m. PO_4.

Spectrographic analysis of the residue of 1 liter of the purified base nutrient solution showed it to contain, in milligrams, about 0.01 aluminum, 0.01 boron, 0.02 copper, 0.01 iron, 0.1 silicon, and 0.1 strontium. No other micronutrients were detected.

Twenty-two cultures were set up. A series of differential treatments involving various aluminum and minor-element combinations, as outlined in table 1, were then added to the purified base nutrient solution.

New solutions were prepared every month. The volumes of the cultures were kept constant by the addition of redistilled water from an all-glass still (4). The pH was maintained between 4.5 and 5.0 by the addition of redistilled HNO_3, and the PO_4 was kept approximately constant by frequent determinations and adjustments with KH_2PO_4.

The plants had been grown in the base nutrient solution since January, 1939, in order to get them well started. When the differential treatments were begun, March 8, 1939, the plants were thinned from three to one per jar. The plants retained were fairly uniform in root and top growth.

All the plants receiving treatments 1 and 2 (base nutrient solution with and without aluminum) developed severe symptoms of manganese deficiency after about 2 months. The aluminum was without effect in this comparison: the plants in cultures 4, 5, and 6, which received 0.1 p.p.m. aluminum, behaved identically as did those in cultures 1, 2, and 3, which received no aluminum.

The plants of treatment 3 (cultures 7, 8, and 9), receiving base nutrient solution plus 0.1 p.p.m. manganese, zinc, and boron and 0.05 p.p.m. molybdenum, made excellent top and root growth. At no time during the experiment did they show symptoms of malnutrition. Companion cultures 10, 11, and 12, which received 0.1 p.p.m. aluminum in addition to the micronutrients named above, showed no tangible signs of either root or top injury, but they did not make such good growth as the cultures without aluminum.

Plants given treatment 5 (base nutrient solution plus 1 p.p.m. manganese, zinc, and boron, 0.5 p.p.m. molybdenum, and 0.1 p.p.m. copper) began to show evidences of injury in about one and one-half months. The roots turned brown, the new laterals were short and became swollen, and the new leaves began to

show iron chlorosis.[3] On the other hand, the plants of treatments 6, 7, and 8, receiving the same minor-element combination as treatment 5 but with additions of 0.1, 0.5, and 2.5 p.p.m. aluminum, respectively, made strikingly better growth.

TABLE 1

Micronutrients added to purified base nutrient solution in which lemon cuttings were grown*

CULTURE	TREATMENT	ALUMINUM	OTHER MICRONUTRIENTS†
		p.p.m.	*p.p.m.*
1, 2, 3	1	0.0	0.0
4, 5, 6	2	0.1	0.0
7, 8, 9	3	0.0	Mn, Zn, B, 0.1 each; Mo, 0.05
10, 11, 12	4	0.1	Mn, Zn, B, 0.1 each; Mo, 0.05
13, 14, 15	5	0.0	Mn, Zn, B, 1.0 each; Mo, 0.5; Cu, 0.1
16, 17, 18	6	0.1	Mn, Zn, B, 1.0 each; Mo, 0.5; Cu, 0.1
19, 20	7	0.5	Mn, Zn, B, 1.0 each; Mo, 0.5; Cu, 0.1
21, 22	8	2.5	Mn, Zn, B, 1.0 each; Mo, 0.5; Cu, 0.1

* Composition of purified base nutrient solution, in milliequivalents per liter: calcium, 6.00; magnesium, 3.71; potassium, 2.79; nitrate, 10.01; sulfate, 2.49.

† Purified iron sulfate was added in uniform amounts to all cultures at a rate of 0.1 p.p.m. iron, three times a week.

Since it was suspected that the toxic effect on plants in cultures 13, 14, and 15 was due to the addition of the copper (0.1 p.p.m.), this element was omitted from culture 13 on May 15, 1939. After about 10 days, new white roots began to emerge on this plant, and shortly thereafter top growth was initiated. From

[3] This is of interest, since it has been shown by the writers (2) that excessive zinc will also induce iron chlorosis in citrus plants grown both in sand and in solution cultures, though provided with ample iron in the nutrient solution.

then on, this plant grew normally, but plants in cultures 14 and 15 became increasingly affected. Hence it is certain that the injury noted was caused by the copper and not by the increases in the other micronutrients. In cultures 16 to 22, however, to which aluminum was added, root growth was virtually indistinguishable from that in the cultures not receiving copper. Pictures of top and root growth of representative plants, showing copper toxicity, recovery when copper was omitted, and the ameliorating effect of aluminum on copper toxicity, are presented in figure 3, A, B, and C, respectively.

These results show that the apparently stimulating effect of small amounts of aluminum on root and top growth, as seen in the experiment with orange cuttings and again demonstrated here, is the result of a detoxifying action on copper.

In 1912, Szücs (9), in studies on the general phenomena of antagonism, showed that the toxic effect of copper sulfate on the geotropic response of the hypocotyl of *Cucurbita Pepo* could be diminished in the presence of aluminum chloride. He employed much higher concentrations of salts than those used in the present studies, however.

Further evidence that the apparently stimulating effect of aluminum, under the conditions of this experiment, was due to its antagonistic influence on copper is afforded by the results in treatments 3 and 4, where low levels of manganese, zinc, boron, and molybdenum were employed in the base nutrient solution and no copper was added. Under these conditions, as noted earlier, the addition of aluminum instead of exerting a stimulating effect actually depressed growth somewhat. Pictures showing the growth of plants in two each of the cultures given low micronutrients, with and without aluminum, are presented in figure 4. There was no evidence of any root abnormality in any of these cultures, but plants receiving 0.1 p.p.m. aluminum did not grow so rapidly as those without aluminum, and the total dry weight of top and roots was somewhat less (see table 2). The copper content of these purified solutions, as revealed by spectrographic analysis, was about 0.02 p.p.m., and it may be that under these conditions aluminum depressed the absorption or utilization of this element and thus brought on an incipient copper deficiency.

The toxicity of aluminum to green plants is well known, and the results of this study suggest that this may be caused, in part, by its depressing influence on the utilization or absorption of copper or of some other essential element.

In this connection, a very curious effect noted with higher concentrations of aluminum (2.5 and 5 p.p.m.) should be mentioned. Lemon cultures 21 and 22 (table 1) were grown for 10 months after the completion of the present experiment. These cultures originally received 2.5 p.p.m. aluminum; culture 22 was subsequently given 5 p.p.m. aluminum. A phenomenal development of roots took place in both, but top growth was retarded. This behavior was evident from the very first. Although none of the other cultures of this experiment were continued for comparison, lemon cuttings of comparable age from another experiment, grown near by in nutrient solutions of almost the same composition but with only 0.5 p.p.m. aluminum, served as a basis of comparison. In figure 5, the "normal" top and root growth of one of these plants (fig. 5, A) is shown in contrast with the greater root development and somewhat depressed top growth

of culture 22 (fig. 5, B). No explanation of this curious behavior is offered; it seems possible, however, that the antagonistic effect of aluminum on copper may have some relation to the root-stimulating effect of aluminum.

EXPERIMENTS TO DETERMINE THE NATURE OR SEAT OF ALUMINUM-COPPER ANTAGONISM

It was noted in this and former studies that with additions of aluminum in concentrations of 0.5 p.p.m. and higher, a precipitate gradually formed in the culture solution, and it seemed possible that the detoxifying effect of aluminum might be no more than a coprecipitation of the copper. In an effort to determine more definitely the nature or seat of the antagonistic effect of aluminum on copper, several tests were made.

Effect of aluminum on copper in culture solutions

Aluminum in the amount of 0.5 p.p.m. was added to a complete culture solution identical with that employed in treatment 5 of experiment 2 (see table 1). The solution was adjusted to pH 5.5, placed in a stoppered bottle, and allowed to stand for a week with occasional shaking. A precipitate appeared during the course of this period, but colorimetric tests for copper in the supernatant liquid showed as much copper where aluminum had been added as in similarly treated solutions from which aluminum had been omitted. This finding indicates that the detoxifying effect of the aluminum is the result of some direct action on or in the plant rather than mere coprecipitation in the culture solution.

Spectrographic analyses

In order to determine the effect of the aluminum on the copper and aluminum content of various parts of the plant, spectrographic analyses of various parts of healthy, copper-injured, and aluminum-copper-treated lemon cuttings were made.

One set of plants was harvested June 15, and another, August 19, 1939. The harvested plants were washed thoroughly with distilled water, and plant parts were segregated as follows: leaves, stems, and root bark of all roots $\frac{1}{16}$ inch or more in diameter; inner wood of these roots; and fine roots. All tissues were then air-dried and weighed. The leaves were broken up by hand; the stems, root wood, root bark, and fine roots were cut into small pieces with clean steel pruning shears; and samples were weighed out for analysis. Aliquots of the plant material were ashed in silica dishes at a temperature of 500°C. until the weight of ash was nearly constant. The ash was thoroughly mixed by grinding, and weighed amounts were mixed with sodium sulfate and suitable reference elements and then arced. A grating spectrograph was used, and the densities of the lines of the different elements were measured in a photoelectric densitometer.[4] By comparing the densities of the measured lines with those obtained by

[4] The spectrograph and densitometer employed in these tests were manufactured by the Applied Research Laboratory, 4336 San Fernando Road, Glendale, California.

arcing standard powders, the concentrations of the different elements were calculated.[5]

The results of the spectrographic analyses are shown in table 2. Though the data on the other micronutrients are perhaps of no special significance as regards the aluminum-copper relationship, they are included to show the distribution and the amounts of the various elements detected. These were the only elements found by direct arcing of the ash of the various citrus parts.

It will be noted (table 2) that, though additions of aluminum to the culture solution, in concentrations of 0.1 and 0.5 p.p.m., increased the aluminum content of root bark and fine roots enormously and slightly increased the aluminum content of root wood, they did not significantly affect the aluminum content of stems or leaves. It is possible that the high concentrations of aluminum in the fine roots and root bark may be accounted for by the presence of difficultly removable precipitate, but it seems more likely that part of this element is in chemical combination with the root tissue, in view of the well-known ability of proteins to fix metals.

With regard to copper, the seat of toxicity is probably localized in the roots, for, as will be noted (table 2), the copper content of the stems and leaves of the noninjured plants (cultures 9, 10, 11, 12, 19, 20) is of the same order of magnitude as that of the copper-injured plants (cultures 14, 15). The antagonizing influence of the aluminum apparently is not in preventing the copper from becoming fixed or absorbed by the plant roots, since the copper content, though slightly lower in the fine roots and root bark of the aluminum-antagonized plants than in the copper-injured plants, does not seem sufficiently low to account for the striking effects of the aluminum. It appears more probable that the presence of aluminum in some manner prevents the copper from exerting its poisonous effect without necessarily preventing the absorption of copper by the root.

The spectrographic analyses (table 2) showing the effect of the addition of aluminum to the culture solution on the aluminum content of the various plant fractions and the observation that higher levels of aluminum stimulated root development at the expense of top growth suggest that if aluminum is a necessary plant nutrient, its function may possibly be more concerned with root development than with top growth. It is interesting, also, to note that, although the purified cultures to which no aluminum was added contained but 0.005 to 0.01 p.p.m. of this element, the lemon plants accumulated substantial quantities from this low concentration. From these results it seems certain that if aluminum is essential for citrus growth, it will be necessary, in order to demonstrate its essentiality, either to reduce the aluminum content of the culture solution below 0.005 p.p.m. or to employ some element which nullifies it, in order to produce deficiency effects.

The spectrographic analyses for the other elements (table 2) are of interest in showing the number of elements present in detectable quantities, as well as the

[5] A spectrographic method for quantitative determination of some 35 elements in citrus ash has been developed by A. P. Vanselow. Data are on file at the University of California Citrus Experiment Station.

TABLE 2

Effect of aluminum and other micronutrient variations on composition of lemon cuttings grown in solution cultures

CULTURES*	TREATMENT† Number	TREATMENT† Aluminum	CONDITION OF PLANTS	AVERAGE DRY WEIGHT PER PLANT	CONSTITUENTS,‡ IN P.P.M. DRY MATTER: Ash	Al	Cu	Zn	B	Mn	Pb	Fe	Mo	Sn	Ni	Sr	Ba	Cr	Total micronutrients
		p.p.m.		*gm.*															
Leaves																			
9	3	0.0	Healthy	94.0	91,300	28.0	5.5	0.0	100.0	27.0	2.7	82.0	1.8	2.7	0.0	22.0	2.3	0.3	274.3
10, 11, 12	4	0.1	Healthy	75.2	90,300	10.0	9.0	0.0	97.0	27.0	2.7	99.0	2.3	0.0	0.0	16.0	1.8	0.2	265.0
14, 15	5	0.0	Copper-injured	13.5	73,600	25.0	5.2	15.0	88.0	66.0	1.5	52.0	7.4	2.2	0.7	21.0	5.2	0.0	289.2
19, 20	7	0.5	Healthy	50.8	122,900	22 0	7.4	37.0	150.0	74.0	2.5	43.0	37.0	0.0	0.0	41.0	5.0	0.0	418.9
Stems																			
9	3	0.0	Healthy	71.6	40,000	5.6	10.0	8.0	36.0	6.8	2.0	18.0	0.8	0.0	0.0	9.2	1.2	0.0	97.6
10, 11, 12	4	0.1	Healthy	43.9	43,700	7.0	8.0	12.0	26.0	7.9	2.2	48.0	0.9	0.0	0.0	32.0	1.3	0.0	145.3
14, 15	5	0.0	Copper-injured	9.4	39,900	8.8	8.0	15.0	40.0	32.0	3.2	12.0	12.0	0.0	0.0	19.0	1.2	0.0	151.2
19, 20	7	0.5	Healthy	21.6	62,700	5.6	7.0	19.0	25.0	9.0	2.5	11.0	9.0	0.0	0.0	25.0	1.3	0.0	114.4
Root wood																			
9	3	0.0	Healthy	14.7	14,900	4.5	4.9	2.1	300.0	1.5	6.0	8.0	1.9	0.0	0.0	2.2	0.4	Trace	331.5
10, 11, 12	4	0.1	Healthy	8.0	14,900	5.2	4.8	2.5	150.0	1.2	4.5	10.0	1.9	0.9	0.0	2.7	0.3	0.0	184.0
14, 15	5	0.0	Copper-injured	3.7	11,600	3.5	5.0	2.7	410.0	2.0	8.1	4.0	23.0	0.0	0.0	1.9	0.2	0.0	460.4
19, 20	7	0.5	Healthy	5.4	18,300	9.2	9.2	3.7	380.0	3.7	3.7	6.0	37.0	0.0	0.0	3.3	0.5	0.0	456.3
Root bark																			
9	3	0.0	Healthy	6.8	102,700	92.0	18.0	24.0	310.0	10.0	21.0	160.0	8.2	4.1	0.0	31.0	3.1	0.0	681.4
10, 11, 12	4	0.1	Healthy	4.0	111,500	340.0	20.0	45.0	250.0	20.0	34.0	310 0	12.0	6.7	0.0	23.0	5.6	0.0	1,066.3
14, 15	5	0.0	Copper-injured	2.2	87,000	110.0	39.0	61.0	610.0	57.0	70.0	780.0	170.0	3 5	Trace	35 0	2.6	0.0	1,938.1
19, 20	7	0.5	Healthy	2.8	87,500	700.0	22.0	88.0	530.0	35.0	53.0	110.0	220.0	Trace	0.0	22.0	1.8	0.0	1,781.8
Fine roots																			
9	3	0.0	Healthy	26.0	93,000	280.0	93.0	120.0	110.0	280.0	140.0	370.0	19.0	4.7	0.0	28.0	2.8	0.0	1,447.5
10, 11, 12	4	0.1	Healthy	15.9	97,200	970.0	78.0	180.0	340.0	240.0	580.0	240.0	130.0	6.8	Trace	15.0	1.9	0.0	2,781.7
14, 15	5	0.0	Copper-injured	1.6	88,500	350.0	890.0	3,100.0	2,700.0	710.0	890.0	1,800.0	2,200.0	8.0	0.0	8.9	1.8	0.0	12,658.7
19, 20	7	0.5	Healthy	9.4	100,800	1,000.0	710.0	1,000.0	810.0	610.0	150.0	200.0	1,300.0	Trace	0.0	9.0	1.5	0.0	5,790.5

* Cultures 9, 10, 11, and 12 were harvested June 15, 1939; cultures 14, 15, 19, and 20, August 19, 1939.
† See table 1.
‡ No measurable quantities of cobalt were found, though a trace was evident in the root bark of cultures 19 and 20.

concentration and distribution of these elements in the plant. Zinc, boron, manganese, iron, and molybdenum were found, as were aluminum and copper, in relatively higher concentrations in fine roots and root bark than in root wood, stems, and leaves. Boron accumulated in the leaves, stems, and root wood to a much greater extent, however, than the other elements. The fact that boron does not form precipitates at low concentrations in culture solutions, as do aluminum, copper, zinc, and the others, and yet was found in high concentrations in the fine roots and root bark tends to confirm the belief that the root accumulations noted are due to chemical combination with the root tissue rather than to precipitates adhering to the root surface.

Only traces of nickel, cobalt, and chromium were found in these plants; this indicates that these elements did not occur as appreciable contaminants under the conditions of this experiment. Measurable amounts of tin, appreciable amounts of strontium and barium, and substantial amounts of lead were found, however. It is of interest to note that strontium and barium, unlike the other metals, were not appreciably fixed by the fine roots and root bark.

SUMMARY

The results of the experiments described herein have shown that an apparently stimulating effect of aluminum on citrus growth is due to the antagonistic effect of aluminum on copper. In the absence of aluminum, 0.1 p.p.m. copper was decidedly toxic to Valencia orange cuttings and to lemon cuttings. The addition of 0.1 p.p.m. aluminum to cultures injured by such a concentration of copper was sufficient to offset this toxicity.

The addition of 0.1 p.p.m. aluminum to purified nutrient solutions containing only a trace of copper and other micronutrients slightly depressed plant growth. It is possible that under these conditions aluminum may have made it difficult for the plants to obtain enough copper or, perhaps, other elements for normal development. This may account, in part, for the depressing effects of aluminum noted by so many investigators.

The addition of 2.5 to 5 p.p.m. aluminum to purified base nutrient solutions greatly stimulated root development but depressed top growth. Lower concentrations of aluminum, that is, 0.1 and 0.5 p.p.m., did not produce this effect, although, as noted previously, total plant growth was somewhat reduced. The cause of this curious behavior is unknown.

Spectrographic analyses of various parts of lemon cuttings grown in solution cultures containing different concentrations of aluminum and copper, indicate that the detoxifying influence of aluminum on copper is seated in the roots. Aluminum does not prevent the absorption of copper by the roots but does, in some manner, prevent injury by this element.

In the absence of aluminum, excessive copper causes citrus roots to take on a brownish appearance and to produce short, swollen laterals, which give the roots a dwarfed, knotty, and unhealthy appearance. Subsequent top growth commonly exhibits iron chlorosis.

Though the results of these experiments do not give any definite answer to the question of the essentiality of aluminum for plant growth, they indicate that lemon cuttings can obtain adequate aluminum, if this element be essential, from concentrations as low as 0.005 p.p.m. The stimulating effect on root growth, at the expense of top growth, when 2.5 to 5 p.p.m. aluminum is added to culture solutions, as well as the antagonistic effect of aluminum on copper, demonstrates that aluminum pronouncedly affects physiological activity in plant roots.

From the results reported in this paper it is evident that mere stimulation of plant growth by the addition of any element to a culture solution does not demonstrate the essentiality of that element. The antagonistic effect of a trace of one element upon another may profoundly influence plant growth and yet mean nothing with regard to essentiality.

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THE THERMAL METHOD AS A QUANTITATIVE MEASURE OF CLAY MINERAL CONTENT[1]

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The minerals found in the clay fraction of soils have been the subject of much study recently and have been shown to be important in determining many soil characteristics, such as base-exchange phenomena, soil structure, permeability, and fertility. Mineralogical studies are particularly useful in soil genesis investigations, since they are indicative of the present status of the weathering processes.

Methods are available by which the major constituents of the clay fraction of soils may be identified. The methods that can be used for the identification of clay minerals have been listed and reviewed by Nagelschmidt (6) and by Hendricks and Alexander (4). Ordinarily, the use of several methods is most effective for complete characterization of the soil clay fraction.

The differential thermal method is one of the methods for the study of clay minerals that have received recent attention. The procedures followed and the apparatus used in this method have been described by Norton (7) and by Hendricks and Alexander (4). In the differential thermal analysis, the sample being studied is heated simultaneously with an inert material. The temperature differences between the two materials and the temperature of the inert material are measured repeatedly. When the temperature difference is plotted as a function of the temperature of the inert material, the resulting curve indicates the temperatures at which endothermic or exothermic reactions occur. The differential thermal method was used recently by Alexander, Hendricks, and Nelson (1) and by Russell and Haddock (8) for the identification of clay minerals in soils.

The suitability of the thermal method as a quantitative measure of several clay minerals occurring in soils has been investigated and is reported herein.

MATERIAL AND METHOD

The pure clay minerals used in this investigation were montmorillonite, kaolinite, hydrated halloysite, halloysite, and illite.[3] Before being used the samples of clay minerals were ground in an agate mortar to pass a 60-mesh sieve. The calcium-saturated clays were obtained by leaching the samples with an excess of

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[3] Sources of the samples were: montmorillonite 1. Island of Ponza, S. B. Hendricks, 2. Smith Co., Mississippi, 3. Wyoming, known commercially as volclay; kaolinite, R. C. Vanderbilt Co., Bath. S. C.; hydrated halloysite, S. B. Hendricks; halloysite, variety indianaite, Ward's Natural Science Establishment; illite, R. E. Grim.

normal calcium acetate followed by repeated washing with a 70 per cent alcohol solution to remove the excess salts. The hydrogen-saturated clays were obtained by electrodialysis. Following each of these treatments the samples were dried and again ground to pass a 60-mesh sieve. The minerals were then brought to moisture equilibrium with an atmosphere having a relative humidity of 37 per cent which was attained in desiccators containing a 50 per cent aqueous solution of H_2SO_4.

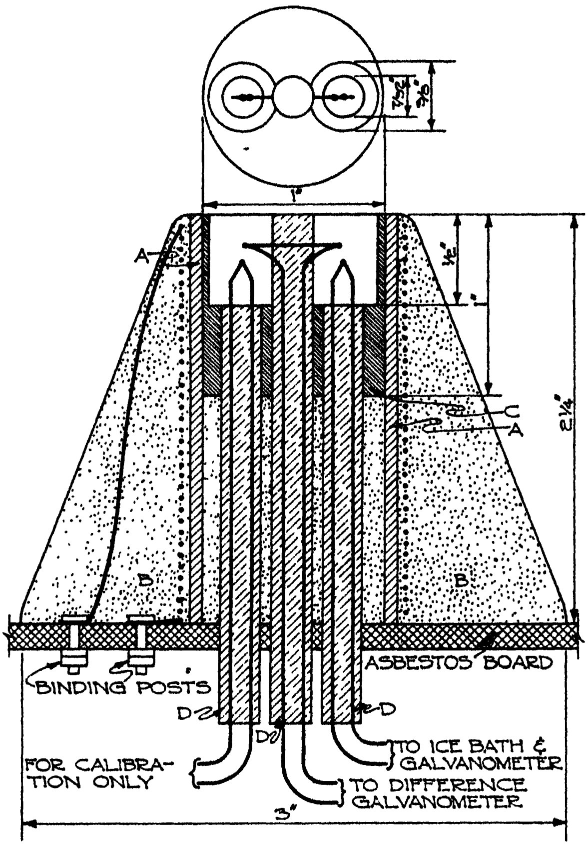

FIG. 1. APPARATUS FOR DIFFERENTIAL THERMAL ANALYSIS

The apparatus used for obtaining the thermal curves of the clay minerals was similar to that described by Russell and Haddock (8), but several changes in its construction were made. A sketch of the apparatus is shown in figure 1. The cylindrical 660-watt heating element *A* was mounted permanently, with refractory cement *B*, around the nickel-steel block *C* containing the sample holes. A lid of the same material was used to cover the sample holes. For insulation, a removable 10-inch hemispherical shell made of a mixture of cement and asbestos was placed over the top of the apparatus. The temperature and the temperature difference were measured with 24-gauge chromel-alumel thermocouples which

entered the metal block through the double-bore $\frac{7}{32}$-inch alundum tubes *D*. The thermocouples were connected to galvanometers, the deflections of which were calibrated by suitable resistances. The alundum tube for the difference thermocouple was mounted in the center of the block. One junction of this thermocouple was centered in each sample hole. Two thermocouples which could be used for measuring the temperature were supplied, one for each sample hole. In any determination only the one in the sample hole containing the inert material was used. One junction of this thermocouple was brought into the sample hole from the alundum tube at the bottom; the other junction was placed in a vacuum bottle containing melting ice. To calibrate the sample temperature thermocouple both holes were filled with alumina and the thermal e.m.f. of the other thermocouple was measured as the system was heated. A heating rate of approximately 22°C. per minute was maintained for each determination by manual control of a variable resistance in series with the heating element. The deflections of the two galvonmeters were recorded as the materials were heated.

For each determination with a pure mineral, a sample of 0.4 gm. was weighed from the material in equilibrium with the atmosphere of 37 per cent relative humidity. A 0.4-gm. sample of the inert material, oven-dry calcined alumina, was weighed for each determination. Dilutions were made with calcined alumina for determinations with smaller amounts of the minerals. The desired amount of mineral for the dilution was weighed and thoroughly mixed with enough of the calcined alumina to make the total weight of the sample 0.4 gm. In a few cases less than 0.4 gm. of mineral, unmixed with alumina, was used. For these determinations sufficient alumina was placed on top of the sample to fill the sample hole. Various proportions of minerals were used for determinations with mixtures of minerals, but in each case a total of 0.4 gm. of material from the atmosphere of 37 per cent relative humidity was used.

It was found in making the determinations that it was essential to use the lid on the sample block. In addition, it was necessary each time to have the sample holes completely filled; otherwise the materials did not heat evenly and the thermal curve was found to drift away from the zero line.

The areas of the peaks for the various curves were obtained by plotting the data for the desired part of the curve on a large scale and measuring the area with a planimeter. These areas depend upon the method of plotting and accordingly should be used only for comparison of one curve with another.

DISCUSSION OF RESULTS

Pure minerals

Thermal curves for both hydrogen-saturated and calcium-saturated clay minerals are shown in figure 2. A description of the curves in figures 2, 3, and 4 is given in table 1. No curves were obtained for a calcium-saturated sample of montmorillonite No. 3 (volclay) or a hydrogen-saturated sample of halloysite. For each of the other minerals there are curves for both hydrogen-saturated and calcium-saturated materials. These curves are characteristic for each of the minerals and can be readily duplicated.

An examination of the curves indicates that there is little difference between the curves for hydrogen-saturated and calcium-saturated minerals except in the

TABLE 1

Description of the curves in figures 2, 3, and 4

CURVE NUMBER	AMOUNT	BASE STATUS	MINERAL
	gm.		
31	0.4	Ca-saturated	hydrated halloysite
33	0.4	Ca-saturated	halloysite (indianaite)
35	0.4	Ca-saturated	montmorillonite #1
41	0.4	H-saturated	montmorillonite #1
42	0.4	H-saturated	kaolinite
43	0.4	H-saturated	hydrated halloysite
44	0.4	Ca-saturated	illite
48	0.4	H-saturated	illite
54	0.4	Ca-saturated	montmorillonite #2
62	0.2	Ca-saturated	hydrated halloysite + 0.2 gm. calcined alumina
63	0.3	Ca-saturated	hydrated halloysite + 0.1 gm. calcined alumina
67	0.4	Ca-saturated	kaolinite
68	0.4	Ca-saturated	hydrated halloysite
72	0.2	Ca-saturated	kaolinite + 0.2 gm. calcined alumina
73	0.1	Ca-saturated	hydrated halloysite + 0.3 gm. calcined alumina
75	0.3	Ca-saturated	kaolinite + 0.1 gm. calcined alumina
98	0.1	Ca-saturated	kaolinite + 0.3 gm. calcined alumina
102	0.2	Ca-saturated	kaolinite + 0.2 gm. Ca-saturated hydrated halloysite
105	0.2	Ca-saturated	hydrated halloysite + 0.2 gm. Ca-saturated montmorillonite #2
113	0.1	Ca-saturated	kaolinite + 0.3 gm. Ca-saturated hydrated halloysite
115	0.3	Ca-saturated	kaolinite + 0.1 gm. Ca-saturated hydrated halloysite
118	0.1	Ca-saturated	hydrated halloysite + 0.3 gm. Ca-saturated montmorillonite #2
119	0.3	Ca-saturated	hydrated halloysite + 0.1 gm. Ca-saturated montmorillonite #2
128	0.3	Ca-saturated	montmorillonite #2 + 0.1 gm. calcined alumina
129	0.2	Ca-saturated	montmorillonite #2 + 0.2 gm. calcined alumina
131	0.1	Ca-saturated	montmorillonite #2 + 0.3 gm. calcined alumina
138	0.4	H-saturated	montmorillonite #3
155	0.3	Ca-saturated	kaolinite + 0.1 gm. Ca-saturated montmorillonite #2
157	0.2	Ca-saturated	kaolinite + 0.2 gm. Ca-saturated montmorillonite #2
158	0.1	Ca-saturated	kaolinite + 0.3 gm. Ca-saturated montmorillonite #2
195	0.4	H-saturated	montmorillonite #2

case of the montmorillonite samples. For this mineral it will be noted that the low-temperature endothermic peak is affected by the type of base saturation.

The curves for kaolinite, 42 and 67, are characterized by the large endothermic reaction for which the peak occurs at 620°C. This endothermic reaction is caused by the loss of the crystal lattice water. There is very little change at low temperatures, which indicates that the kaolinite absorbs little water in equilibrium with the atmosphere of 37 per cent relative humidity. The sharp exothermic break in the curve at 1000°C. is caused by the recrystallization of the aluminum oxide.

The hydrated halloysite curves, as indicated by 43 and 68, have more endothermic peaks than the kaolinite curves. There is a large endothermic break

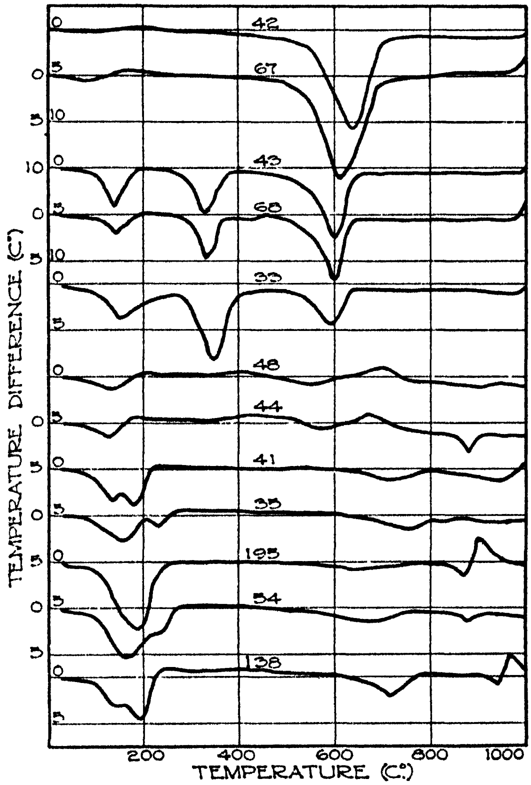

Fig. 2. Thermal Curves for Calcium- and Hydrogen-Saturated Clay Minerals

with a peak at 595°C. and also a smaller endothermic peak at 330°C. The areas of these two peaks were measured for a number of determinations and in all cases the ratios of the areas of the two peaks remained the same. The small peak of 140°C. indicates that hydrated halloysite has more surface-absorbed water than kaolinite. The exothermic reaction for the recrystallization of aluminum oxide occurs at the same temperature as for kaolinite, but the peak is smaller. A sample of the hydrated halloysite was oven-dried at 110°C. for 12 hours, a treatment which, according to Hendricks (3), should change it to halloysite. After the sample was allowed to come to moisture equilibrium with an atmosphere of

37 per cent relative humidity, however, the thermal curve obtained did not differ materially from that of the undried mineral.

The thermal curve for halloysite (indianaite), 33, is similar in form to that of the hydrated halloysite. The size of the two endothermic peaks, however, is reversed. In the curve for halloysite the larger of the two endothermic peaks comes at a lower temperature. The temperatures at which the two peaks occur are 340° and 575°C. The ratio of the areas of the two peaks also remained constant for all determinations with the mineral. A sample of this mineral was

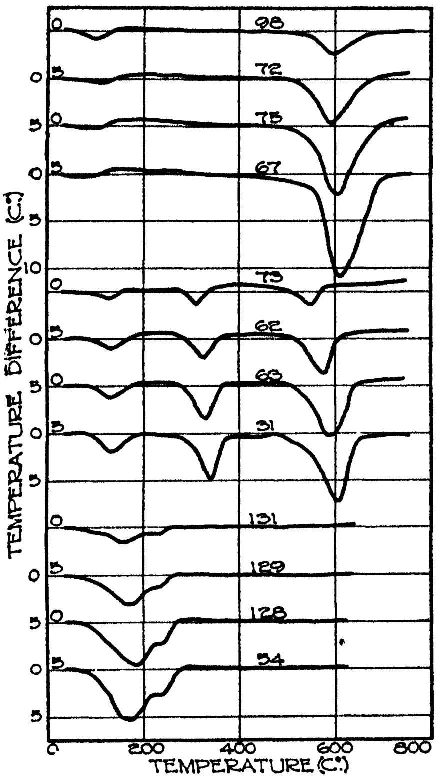

FIG. 3

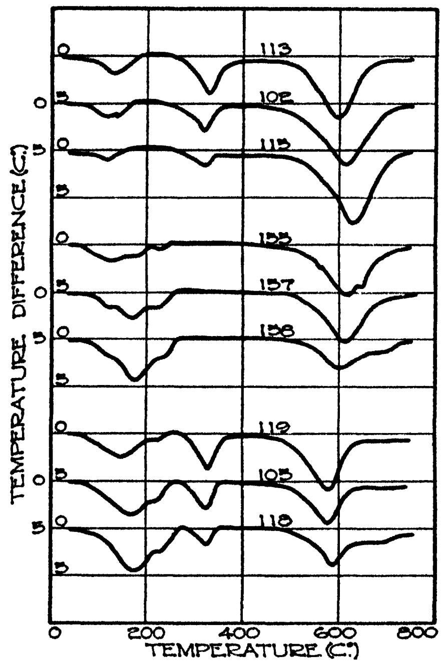

FIG. 4

FIG. 3. THERMAL CURVES FOR CLAY MINERAL DILUTIONS
FIG. 4. THERMAL CURVES FOR CLAY MINERAL MIXTURES

also dried for 12 hours at 110°C., but no difference was obtained in the thermal curve.

Alexander and Hendricks (2) recently reported the occurrence of gibbsite in association with kaolinite in the weathering crusts of rocks from the southeastern United States. This mineral has an endothermic peak at about 320°–350°C. which is similar to one of the endothermic peaks obtained for hydrated halloysite and indianaite. It is possible that the samples herein designated as hydrated halloysite and halloysite (indianaite) may be mixtures of kaolinite and gibbsite in different proportions.

Thermal curves are given for three samples of montmorillonite. It will be noted that the curves for hydrogen-saturated material are distinctly different from those saturated with calcium. The characteristic feature of the montmorillonite is the endothermic loss of water at low temperatures. This endothermic effect is due to the loss of the water absorbed between the layers of the montmorillonite.

The curves for the two calcium-saturated samples, 35 and 54, are very similar and both show a smaller endothermic reaction at about 225°–235°C., as well as the larger endothermic reaction at a lower temperature. The two samples vary somewhat in the temperatures at which the peaks occur and also in the size of the peaks. The curves for hydrogen-saturated montmorillonite also agree well with one another. For two of the samples, 41 and 138, the curves show two definite peaks, the larger one occurring at a temperature of 180°–190°C. and the smaller at a temperature of 140°–150°C. Though the curve for the Mississippi montmorillonite, 195, does not have two definite peaks, the shape indicates that the same endothermic reactions occur, the larger at a temperature of 190°C. The effect of various cations on the low-temperature part of the montmorillonite curve has been investigated by Hendricks, Nelson, and Alexander (5), who assert that the lattice water of montmorillonite is held by several different forces and that the water held by the strongest forces causes the endothermic peaks at higher temperatures. Their results indicate that the peak at 225°–235°C. in the curves for calcium-saturated material is caused by the loss of water hydrating the calcium ions, and that lattice water causes the lower peak. For montmorillonite saturated with hydrogen it was indicated that the cation was not hydrated, the different endothermic peaks being caused by separate layers of lattice water. An additional difference between the curves for montmorillonite saturated with hydrogen and those saturated with calcium may be noted. All of the curves for hydrogen-saturated material have an exothermic peak between 900° and 1000°C. which is not present in any of the curves for calcium-saturated material.

The thermal curves for illite are not so useful for their identification as are those of the other minerals. Though the curves obtained are characteristic for the mineral and are reproducible, they do not have striking features that serve to identify the curve. The curves for hydrogen-saturated and calcium-saturated illite are very similar.

The temperatures at which the endothermic peaks of the various curves occur differ slightly from those reported by other investigators. This may be attributed to the method by which the sample temperature was measured. In these studies the sample temperature was measured by a thermocouple inserted in the inert material rather than by one mounted in the center of the metal block, as has been described by other workers (4, 7, 8).

Dilutions of minerals

The thermal curves for each of the clay minerals except illite have an endothermic peak or peaks at definite temperatures that are characteristic for the mineral. The size of each of these peaks depends upon the amount of mineral

used. Dilutions of the minerals with alumina were made in order to obtain curves for small samples of mineral and yet have the sample hole completely filled. In table 2 data are given concerning the size of the peaks for the several

TABLE 2

Effect of dilution on the area of the characteristic endothermic reactions of calcium-saturated clay minerals

AMOUNT OF MINERAL USED	MONTMORILLONITE #2			KAOLINITE			HYDRATED HALLOYSITE					
	180°C.			600°C.			320°C.			580°C.		Ratio 580/320
	Curve Number	Measured area	Area per gram	Curve Number	Measured area	Area per gram	Curve Number	Measured area	Area: per gram	Measured area	Area per gram	
gm.												
	93-1	15.2	37.9	66	22.7	56.8	65	5.88	14.7	13.2	33.0	2.24
	93-2	14.8	37.0	67	23.3	58.3	68	5.92	14.8	13.9	34.8	2.35
	54	16.0	40.0	86	23.0	57.4	83	5.60	14.0	13.2	33.1	2.36
0.4	107	15.9	39.8	101	24.2	60.5	85	5.23	13.2	12.8	32.0	2.42
	145	15.4	38.6				39*	4.60	11.5	8.87	22.2	1.93
	122†	16.4	40.9									
	123†	16.3	40.8									
				95	16.0	53.4	84‡	4.97	16.6	10.4	34.6	2.09
0.3				97	15.5	51.7	87‡	4.74	15.8	9.54	31.8	2.01
				99§	17.6	58.7	88	4.58	15.3	10.2	33.9	2.22
				100§	17.1	57 0						
0.3 plus alumina	128	12.4	41.3	75	16.2	54.0	63	3.87	12.9	9.11	30.4	2.35
	139	12.3	41.0	76	17.3	57.7	64	4.07	13 6	9.85	32 8	2.42
							89	4.06	13.5	8.86	29.5	2.18
0.2 plus alumina	129	8.45	42.2	72	10.0	50.0	61	2.73	13.7	6 12	30.6	2 24
	140	8.38	41.9	74	10.4	52.0	62	2.77	13.9	6.64	33.2	2.40
	131	4.03	40.3	78	5.22	52.2	60	1.12	11.2	2.66	26.6	2.36
	141	4.78	47.8	98	4.00	40.0	73	1.14	11.4	2.63	26.3	2.31
0.1 plus alumina	142	5.12	51.2	108	3.21	32.1	125‖	2.95	29.5	7.11	71.1	2.41
	144	5.08	50.8	121‖	8.59	85.9						
	148	4.13	41.3	124‖	8.70	87.0						
	149	4.16	41 6									

* Dried at 100°C. and placed in atmosphere of 37 per cent relative humidity.

† Montmorillonite #2 before calcium saturation.

‡ Sample hole not filled, strong zero line slope.

§ Mineral packed into the sample hole and covered with enough alumina to fill the hole.

‖ Sample concentrated at the thermocouple.

minerals when samples of different sizes are used. Curves representative of those dilutions are shown in figure 3.

For each of the minerals it will be noted that the areas of the peaks for the different-sized samples fall within narrow limits. The areas of the endothermic peaks of the diluted samples are proportional to the areas of the peaks of the

0.4-gm. samples but, as the dilution of the sample becomes greater, the area of the peak becomes a less reliable measure of the amount of material present. For the smallest samples of kaolinite and hydrated halloysite the areas of the peaks are less than those expected on the basis of the area of the 0.4-gm. sample.

The temperature at which the peak of the endothermic reaction occurs becomes lower as the amount of mineral used is decreased. This is to be expected, since the heating rate is constant for all determinations and the reaction will be completed more quickly for small samples that have less water to be removed than for larger samples.

The area of the endothermic peak for kaolinite appears to increase slightly as a result of packing of the sample. For curves 66, 67, 86, and 101, in which a 0.4-gm. sample was used, it was necessary to pack the mineral slightly to get it all in the sample hole. It was not necessary to pack a 0.3-gm. sample, and the areas for curves 95 and 97 were not quite proportional to that of the 0.4-gm. sample. When, as in curves 99 and 100, a 0.3-gm. sample was packed into the hole, which was then filled with alumina, the area obtained for the peak was proportional to that of the 0.4-gm. sample. It was necessary to pack the 0.3-gm. dilution, and the area agrees well with that of the 0.4-gm. sample. The dilutions of smaller samples were not packed into the hole, and the areas are proportional to that of the 0.3-gm. unpacked sample.

The areas of the peaks for the dilutions of hydrated halloysite are proportional to the amount of mineral used, except for the greatest dilution, for which the areas are smaller than expected. The two peaks of the hydrated halloysite curves are affected equally by dilutions. This is indicated by the constant ratio of the areas of the two peaks for each curve.

The best agreement of the areas of peaks for dilutions was obtained with the sample of calcium-saturated montmorillonite used. Instead of areas of the peaks of the dilution of 0.1-gm. samples being low in proportion to the areas of the 0.4-gm. samples, as for kaolinite and hydrated halloysite, they were slightly higher. The areas of the peaks would be very satisfactory for estimating the amount of this sample of montmorillonite present. Some difficulty was encountered in determining three of the curves for montmorillonite, 141, 142, and 144, and the areas for the peaks of these curves are higher than the areas for the other curves. Since the size of the low-temperature endothermic peak of montmorillonite curves is a function of humidity (5), greater accuracy could be obtained in estimating the concentration of this mineral by first bringing it to equilibrium with an atmosphere having a relative humidity higher than the 37 per cent used in these studies.

The necessity of having the sample thoroughly mixed with the alumina in dilution studies is indicated by the data in table 2 for three curves of kaolinite and hydrated halloysite, 121, 124, and 125. In the determination of these curves, the sample, instead of being mixed with the alumina, was concentrated at the thermocouple with enough alumina below and above the sample to fill the sample hole. It can be seen that the areas for the peaks of these curves are much larger than those obtained for samples uniformly distributed through the sample hole.

Mineral mixtures

After the areas of the peaks for dilutions of the different minerals had been obtained, thermal curves were determined for known mixtures of clay minerals in order to determine the feasibility of identifying minerals quantitatively in mixtures. In table 3 are given data for the measurement of the areas of the peaks of the thermal curves of mineral mixtures. Curves determined for the mineral mixtures used are shown in figure 4.

The mineral mixtures for which curves have been obtained are kaolinite and hydrated halloysite, kaolinite and montmorillonite, and montmorillonite and hydrated halloysite. Duplicate curves were not obtained for mixtures of montmorillonite and hydrated halloysite. The areas of the endothermic peaks of the curves of these mixtures were measured by the same method as before. After the measurements had been obtained, the amount of each mineral present was calculated in terms of the areas given in table 2 for pure minerals and compared with the actual amounts. The results of these calculations are also given in table 3.

TABLE 3

Areas of characteristic endothermic reactions of pure mineral mixtures

CURVE NUMBER	AMOUNT OF MINERAL USED			AREA OF CHARACTERISTIC PEAKS					CALCULATED AMOUNTS PRESENT		
	Kaolinite	Montmorillonite	Hydrated halloysite	180°C.	320°C.	Hydrated halloysite	Kaolinite	Total	Kaolinite	Montmorillonite	Hydrated halloysite
	gm.	*gm.*	*gm.*						*gm.*	*gm.*	*gm.*
112	0.10	0.00	0.30		4.60	10.7	3.43	14.1	0.06		0.32
113	0.10	0.00	0.30		4.00	9.28	5.12	14.4	0.09		0.28
114	0.10	0.00	0.30		4.00	9.28	4.87	14.2	0.08		0.28
102	0.20	0.00	0.20		2.52	5.85	10.3	16.1	0.18		0.18
103	0.20	0.00	0.20		2.95	6.85	6.55	13.4	0.11		0.21
104	0.20	0.00	0.20		2.74	6.36	8.74	15.1	0 15		0.19
111	0.20	0.00	0.20		2.83	6.57	9.46	16.0	0.16		0.20
115	0.30	0.00	0.10		1.50	3.48	15.1	18.6	0.26		0.11
116	0.30	0.00	0.10		1.48	3.43	15.1	18.5	0.26		0.10
154	0.30	0.10	0.00	3.89			13.3	13.3	0.28	0.10	
155	0.30	0.10	0.00	3.77			13.4	13.4	0.30	0.10	
171	0.30	0.10	0.00	3.20			11.5	11.5	0.20	0.08	
134	0.20	0.20	0.00	8.04			11.2	11.2	0.19	0.21	
156	0.20	0.20	0.00	8.18			12.7	12.7	0.21	0.21	
157	0.20	0.20	0.00	7.24			11.6	11.6	0.20	0.19	
158	0 10	0.30	0.00	11.5			7.66	7.66	0.13	0.30	
159	0.10	0.30	0.00	11.8			8.40	8.40	0.14	0.30	
118	0.00	0.30	0.10	12.0	1.32	4.31		4.31		0.31	0.09
105	0.00	0.20	0.20	9.20	2.45	5.78		5.78		0.24	0.18
119	0.00	0.10	0.30	6.73	4.05	8.70		8.70		0.17	0.29

The most satisfactory results were obtained with the mixture of kaolinite and hydrated halloysite. Except for curves 103 and 104, the amounts calculated to

be present agree well with the actual amounts present. For mixtures of these two minerals the low-temperature part of the curve is not important. The significant parts of the curve are the peaks at 330° and 600°C. The endothermic reactions near 600°C. for the two minerals come at temperatures so close together that actually only one peak occurs. The temperature of this peak varies between the temperatures of the peaks for the two minerals, depending upon which of the minerals predominates. The 330° peak serves to identify the hydrated halloysite. The average value of 2.32 for the ratio of the two peaks of hydrated halloysite was used to determine the part of the 600° peak due to hydrated halloysite. The area of the 320° peak was multiplied by 2.32 and then subtracted from the measured area of the 600° peak. The remaining area was attributed to kaolinite. By this method the 600°C. peak was resolved into its component parts so that the areas could be used for estimating the amount of each mineral present.

In the curves for mixtures of montmorillonite and kaolinite, the low-temperature peaks of montmorillonite agree well with those of the montmorillonite dilutions. In all of the mixtures the calculated amount of montmorillonite agrees with the actual amount. The agreement for kaolinite, however, is not as good. Only for the mixture of 50 per cent kaolinite do the calculated amounts agree well with the actual amounts present.

Of the montmorillonite–hydrated-halloysite mixtures, only in the one with 75 per cent montmorillonite and 25 per cent hydrated halloysite do the calculated amounts check with the actual amounts. The temperatures at which some of the endothermic reactions for montmorillonite and hydrated halloysite occur are so similar that the thermal curves overlap. The hydrated halloysite has a small low-temperature peak which interferes with that of montmorillonite; the low-temperature peak of montmorillonite carries over to the beginning of the 330° peak of hydrated halloysite, and the montmorillonite curve drops below the zero line above 600° to interfere with the 600° peak of hydrated halloysite. Since no satisfactory method of separating these common peaks was available, the accurate estimation of the composition of montmorillonite–hydrated-halloysite mixtures was impossible. It will be noted that the ratios of the areas of the two peaks of hydrated halloysite do not agree with the ratios obtained for the pure mineral.

SUMMARY

Thermal curves have been determined for several clay minerals, dilutions of the minerals, and mixtures of the clay minerals. An attempt has been made to estimate quantitatively the amount of each clay mineral present, first by measuring the areas of endothermic peaks of the curves of pure minerals and dilutions of the minerals and then by measuring the areas of the endothermic peaks of mixtures of the clay minerals.

Each of the clay minerals has a characteristic thermal curve which is useful for the identification of the mineral. The curve of each mineral can be reproduced readily. There are, however, small variations in the curves of different

samples of the same mineral. This is indicated by the curves of the three samples of montmorillonite, which are of the same character but are not identical. Since the thermal curves of montmorillonite are affected by the exchangeable bases present, it is important to know the base status of a mineral mixture when interpreting its thermal curve.

The thermal curves for hydrated halloysite and halloysite were found to have two distinct endothermic reactions occurring at the same temperatures. For each of these minerals the ratio of the areas of the two peaks was found to remain constant for all determinations. The ratio of the areas could be used for determining the area of one peak if the area of the other peak was known. The endothermic peak at 320°–350°C. for these two minerals occurs at the same temperature as does an endothermic peak of gibbsite.

Thermal curves were determined for dilutions of the clay minerals with alumina in order to obtain curves of small samples for comparison with the curves of pure minerals. The areas of the endothermic peaks were measured and found to be proportional to the areas of the peaks of the pure minerals. The agreement was particularly good for the sample of montmorillonite used. The areas of the peaks were less reliable for the small samples of kaolinite and hydrated halloysite.

The areas of the endothermic peaks of thermal curves of clay mineral mixtures were obtained and used for estimating the amounts of each of the minerals present. Good agreement with the actual amounts present was obtained for the kaolinite–hydrated-halloysite mixture and for montmorillonite in the montmorillonite-kaolinite mixture. Thermal curves of the montmorillonite–hydrated-halloysite mixture were not satisfactory for estimating the amounts present.

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FIELD STUDIES ON METHODS FOR DETERMINING AVAILABILITY OF SELENIUM TO PLANTS[1]

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Since the discovery that certain soils contain selenium in amounts large enough to cause vegetation growing on these soils to be toxic, work has been in progress at this laboratory to develop a practical method for mapping seleniferous land. It has already been shown that the total selenium content of the surface soil is no index to the amount of selenium that plants growing in the soil will absorb (1). Therefore the analysis of surface soils for total selenium is of little value in this respect. In earlier studies (2, 4, 5) it was demonstrated that certain geological formations are highly seleniferous and that on weathering they form soils which produce toxic vegetation. For reconnaissance work, therefore, the mapping of these geological formations serves in locating areas which are "generally" seleniferous. Several factors, however, cause variations in the selenium content of the vegetation growing within these areas (4), and for detailed work other methods must be applied.

It was thought that a method for determining the "available" selenium in soils would be of value in detailed mapping. Greenhouse studies on methods have shown that the water-soluble and the base-soluble selenium contents of the soils used were relatively accurate measures of the availability of the selenium to plants growing in these soils (6). It was decided, therefore, to make similar studies in the field to establish the reliability of the methods.

EXPERIMENTAL PROCEDURE

Soil and plant collections were made from 10 fenced plots, each 2 rods square, located at random over two sections of land known by its history to produce toxic vegetation. Western wheat grass (*Agropyron smithii* Rydb.) has been collected on several dates for 3 years. The plants were cut off at the surface of the ground, at random over three fourths of each plot, dried at 50–60°C. for 48 hours, finely ground, and analyzed for selenium by the method described by Moxon (3).

Soil samples used in this study are composites of samples made at three locations within each plot. Total selenium was determined on finely ground samples by the method used for plant analysis.

Water-soluble selenium was determined on the finely ground, air-dried soils. Two 500-gm. samples of each soil were placed in 4-liter Erlenmyer flasks, to each of which was added 3 liters of water. The flasks and their contents were

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heated on the steam bath for 5 hours with occasional shaking. After cooling, the flasks were made up to their original volume, as marked on the flask before heating, and the contents of the flasks were again well mixed. After standing a few hours to permit most of the soil to settle out, most of the liquid was filtered off with gentle suction through asbestos, and the two filtrates for each soil were combined. A 5-liter aliquot was treated with 4–5 cc. of 40 per cent NaOH solution and evaporated almost to dryness on a steam bath. Selenium was determined on the residue as described above.

Base-soluble selenium was determined on air-dried, finely ground soil. Samples of 200 gm. each were treated with 0.5 *N* HCl until effervescense ceased. The solution was filtered off with suction, the soil was resuspended in 0.1 *N* HCl, and the solution was again filtered off with suction. This step was repeated with the acid and then with water. The soil was air-dried, finely ground, and stirred for 4 hours with 2 liters of 4 per cent NH_4OH solution containing 5 gm. of

TABLE 1

Selenium content of A. smithii *at 10 locations on various dates*

PLOT NUMBER	SELENIUM CONTENT, IN PARTS PER MILLION								
	June 27, 1939	July 6, 1939	May 27, 1940	June 10, 1940	June 24, 1940	May 17, 1941	June 20, 1941	July 11, 1941	Average
1	23	18	26	32	33	20	20	20	24.0
2	1	tr*	1	tr	2	2	3	2	1.4
3	6	5	3	5	3	3	2	3	3.8
4	3	5	2	2	3	tr	4	2	2.6
5	7	6	9	8	8	8	4	4	6.8
6	tr	tr	tr	tr	tr	tr	tr	tr	tr
7	2	4	3	1	2	tr	tr	2	1.8
8	10	7	11	14	16	20	6	3	10.9
9	8	9	13	12	14	10	9	8	10.4
10	7	6	6	5	7	4	6	3	5.5

* tr = trace (less than 0.5 p.p.m.).

ammonium oxalate. The mixture was then passed through a Sharples supercentrifuge, 1500 cc. of the solution was evaporated to dryness on the steam bath, and the residue was analyzed for selenium as described above.

RESULTS AND DISCUSSION

The results of the plant analyses are given in table 1. The results indicate an annual variation in the selenium content of the plants caused probably by variations in rainfall, but generally the relative availability of the selenium in the various plots remained constant as measured by the selenium in the *A. smithii.* Because of this constancy the average selenium content of the grasses obtained from the data in table 1 is used in this study as an index to the amount of "available" selenium present in the soils studied. These averages are listed in table 2 along with the results of the soil analyses.

It is evident from table 2 that there is no correlation between the selenium content of the grass and the total, water-soluble, or base-soluble selenium con-

tent of the surface foot of soil. The lack of correlation with the two soluble forms of selenium can be explained in at least two ways: First, the methods of extrac-

TABLE 2

Selenium content of A. smithii *as compared to the total, water-soluble, and base-soluble selenium contents of the soils in which it grew*

PLOT NUMBER	DEPTH OF SOIL SAMPLE	TOTAL Se CONTENT OF SOIL	BASE-SOLUBLE Se CONTENT OF SOIL*	WATER-SOLUBLE Se CONTENT OF SOIL*	AVERAGE Se CONTENT OF A. SMITHII
	inches	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
1	0–12	1.5	0.483	<0.005	24.0
	12–24	3.6			
	24–36	5.0			
2	0–12	3.9	0.289	†	1.4
	12–24	3.5			
	24–36	3.9			
3	0–12	1.6	0.360	0.008	3.8
	12–24	1.5			
	24–36	2.4			
4	0–12	3.8	1.190	†	2.6
	12–24	3.7			
	24–36	4.9			
5	0–12	2.1	0.229	0.040	6.8
	12–24	3.8			
	24–36	3.3			
6	0–12	1.2	0.232	†	<0.5
	12–24	1.7			
	24–36	1.4			
7	0–12	2.0	0.228	0.040	1.8
	12–24	1.8			
	24–36	1.7			
8	0–12	4.0	0.354	0.056	10.9
	12–24	4.5			
	24–36	4.5			
9	0–12	1.4	0.640	†	10.4
	12–24	2.4			
	24–36	2.8			
10	0–12	2.4	0.467	0.030	5.5
	12–24	3.2			
	24–36	3.8			

* Analyses on 0–7-inch sample only.

† No analysis made.

tion may be faulty. The methods used here have proved themselves quite reliable, however, under greenhouse conditions, and the results obtained on a

soil are reproducible. If the top foot of soil is responsible, therefore, for the selenium in the plants growing in the soil, these methods of determining "available" selenium should be somewhat more reliable than they have shown themselves to be in this study. This brings up the second possible explanation, that the second and even the third foot of soil is of at least as much importance in this area as the top foot of soil as concerns the selenium content of plants growing in it. A study of the total selenium contents of the soils tends to support this conclusion. Those soils that produce the most toxic vegetation also show the greatest amount of leaching of selenium. Much of the selenium that is leached from the surface soil is undoubtedly "fixed" at lower levels, but it is possible that part of it remains soluble and is therefore available to plants. Data other than those presented here are on hand to substantiate this conclusion. Thus, to avoid erroneous conclusions, it is essential that more than the surface foot of soil be considered in selenium studies such as this.

CONCLUSIONS

From the data presented here it seems that no method of soil analysis will prove a practicable aid in detailed mapping of soils capable of producing seleniferous vegetation, since the second and possibly the third foot of soil must be studied as well as the surface foot. Apparently a much more practical means of establishing the occurrence of seleniferous soil is the analysis of the vegetation growing on it. Further work on this and on the leaching of selenium should be done.

SUMMARY

In field studies on naturally seleniferous soils it has been found that no correlation exists between the selenium content of *A. smithii* and the total, water-soluble, or base-soluble selenium content of the surface foot of the soil in which it grew.

Soils in which the leaching of selenium is apparently the greatest seem to produce plants of the highest selenium contents, and it appears that much selenium is absorbed from the subsurface soils.

The analysis of the plants growing in a soil seems to be the most practicable method of determining the "available" selenium in the soil.

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EROSION LOSSES OF MAJOR PLANT NUTRIENTS AND ORGANIC MATTER FROM COLLINGTON SANDY LOAM[1]

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There has been considerable speculation as to the nature and extent of plant nutrients and organic matter lost through erosion from different soil types under various systems of management. Many of the estimates of nutrients and organic matter lost have been obtained from soil-loss records that are available for several of the important soil types of the United States. The general method of determining nutrient and organic matter losses has been from calculations based on a chemical analysis of the particular soil type. The soil analysis used for the calculations may or may not have been from an area where degree of erosion or previous land use was comparable with the area where run-off determinations were made. The amount of nutrients lost by erosion also has been estimated from an analysis of the soil at different intervals, combined with a determination of losses from crop removal and leaching, the difference being considered to represent erosion losses. Though plant nutrient losses obtained under the aforementioned systems are subject to considerable criticism, it is felt that these estimated figures have done much to present the effect of erosion in depleting soil fertility. The data presented by Lipman (4) on estimated plant nutrient losses from the soils of the United States give striking evidence on this point.

Slater and Carleton (5), in an investigation of organic matter losses through erosion from soil samples obtained from run-off experimental plots at the Clarinda, Iowa, and Bethany, Missouri, Soil Conservation Experiment Stations, found that the amount of organic matter lost through erosion was greater than was indicated from an analysis of the plot soils.

To obtain further information on the problem of plant nutrient and organic matter losses through erosion, the program of the Marlboro Soil Conservation Experiment Station was outlined to include chemical studies of eroded material. This experiment station is in Marlboro, New Jersey, and is a cooperative activity of the New Jersey Agricultural Experiment Station and the Soil Conservation Service.

THE EXPERIMENTAL AREA

The Marlboro Station is located on Collington sandy loam soil. The experimental area has a slope of approximately 3½ per cent, with moderate erosion.

[1] Joint contribution from the Soil Conservation Service, Office of Research, U. S. Department of Agriculture, and the New Jersey Agricultural Experiment Station, New Brunswick, New Jersey. Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

[2] Formerly project supervisor, now senior soil technologist, Office of Experiment Stations; cooperative agent in soil chemistry; and junior soil conservationist, respectively.

The Collington soils are relatively high in inherent productivity. The A_1 horizon is 8 to 10 inches deep and is light brown to reddish brown. The B_1 horizon usually is heavier than the surface soil and varies considerably within comparatively small areas. In some places a relatively high greensand content is reached at a depth of 18 to 24 inches, whereas in others the greensand layer may be found at a depth of 36 or more inches. The Collington soil was selected for experimental run-off studies because it was thought to be typical of the extensive areas of light sandy soil found on the Coastal Plain. A complete chemical and physical analysis of the Collington sandy loam profile from the experimental area is given in table 1.

TABLE 1

Analysis of Collington sandy loam profile from the Soil Conservation Experiment Station, Marlboro, New Jersey

Analyses in percentages

HORIZON	DEPTH	CHEMICAL ANALYSIS*									
		SiO_2	Ti	Fe	Al	Ca	Mg	Na	K	N	P
	inches										
Ap	0–8	82.66	.23	3.18	2.71	.188	.349	.18	.85	.076	.162
A_2	8–22	87.56	.26	2.02	2.69	.104	.174	.22	.71	.023	.049
B_1	22–30	79.99	.22	3.83	3.96	.162	.307	.17	.68	.031	.062
B_2	30–36	81.20	.24	3.57	3.70	.184	.310	.18	.68	.025	043
C	36–	90.51	.28	1.27	2.22	.106	.134	.20	.61	.007	.015

HORIZON	DEPTH	MECHANICAL ANALYSIS†		
		Sand	Silt	Clay
	inches			
Ap	0–8	82.9	6.9	10 2
A_2	8–22	81.6	7.7	10.7
B_1	22–30	71.6	8.1	20.3
B_2	30–36	76.8	6.2	17.0
C	36–	90.3	2.3	7.4

* Soil material prepared for analyses and analyzed according to the methods of the Association of Official Agricultural Chemists (1).

† Bouyoucos method.

Attention is directed to the comparatively low content of silt and clay indicated by the mechanical analysis. The land selected was used for the production of miscellaneous vegetables for several years before it was acquired as an experimental site.

The main agricultural activity of the area is the production of truck crops, potatoes, and fruit. Nearness to large marketing centers and the relatively high inherent productivity of the soil have resulted in high land values. It is estimated that one tenth of the population of the United States is found within a 75-mile radius of the Station. With soil and economic conditions such as these, the maintenance of soil productivity becomes of paramount importance.

EXPERIMENTAL INSTALLATION

The field experiment was designed primarily to determine the effect of additions of organic matter and the use of cover crops on soil and water losses. This approach was selected because the intensive methods of cultivation employed in the Coastal Plain have been exhaustive of soil organic matter. With the depletion of soil organic matter, erosion has been observed to become more serious.

Installation of equipment for measuring soil and water loss from plot areas was completed during June, 1938. Standard run-off equipment, consisting of silt box and Geib divisor with second and third tanks depending on area of plot, was used. The complete field run-off investigations included three slope lengths with four treatments, each treatment being established in duplicate on each slope length, giving a total of 24 plots. Slope lengths are 70, 140, and 210 feet. All plots are 14 feet wide. Treatments under study consisted of a check with no organic matter treatment; cover crop (rye seeded in fall after the vegetable crop was harvested); manure at the rate of 20 tons per acre, applied in spring; and the combined cover crop and manure treatment. All plots receive the same rate of commercial fertilizer annually, the kind and amount depending on the particular crop being grown.

PROCEDURE

In any investigation directed toward a determination of organic matter and plant nutrient losses resulting from erosion, particular attention should be given to the technique of obtaining samples for analysis. Unless the material analyzed is representative of the eroded material, the results are open to question. Obtaining a representative sample of eroded material presents a difficult problem because of variability in erosion conditions. For the purpose of sampling for plant nutrient, organic matter, or any other losses there is no basis for assuming that there is such a thing as a representative storm or a representative period of soil loss during which the taking of samples for analysis will give an accurate figure of actual losses. Records of soil loss as well as numerous observations show conclusively that erosion is not a uniform process but varies with amount and character of rainfall, type of soil, degree of slope, soil treatment, and previous land use. Acknowledging this variability means that any sampling procedure should be so developed that a direct fraction of the soil and water lost from each storm under each treatment is obtained for making the samples for chemical study. From both the field and laboratory standpoint this involves a considerable number of samples. The sampling procedure in this study was as follows:

Field Sampling

The procedure followed will be illustrated by outlining the equipment and methods employed in collecting run-off and obtaining a direct fraction of the run-off for chemical analysis from a 14 by 210-foot plot. The field equipment on this plot consists of a silt box or first tank, a second, and a third tank with a 5–1-inch by 6 inch Geib (2) divisor between the silt box and the first tank and a 11–½-inch by 4-inch divisor between the second and third tanks. All storage

tanks are sheet metal and are provided with a 2-inch drain. In order to prevent silting in the drain as well as provide for more accurate samples, the drain is closed from the inside of the tank with a standpipe extending above the divisor level. The silt box is $3\frac{1}{2}$ feet by 5 feet by 3 inches deep, and the second and third tanks are 4 feet in diameter and 3 feet in depth. With storage tanks as large as these, filled with mixtures of soil and water, it was difficult to obtain a direct fraction of the run-off mixture. In order to overcome this difficulty, a system of sampling twice was worked out; that is, a representative sample was taken from the storage tanks and placed in a smaller container, where the final fractional sample was taken for chemical study.

The procedure for obtaining the representative sample and fractional sample from each of the storage tanks for the various run-off conditions is as follows:

Silt box or first tank. When soil losses are small, the entire contents of the silt box are agitated vigorously and the drain is removed, allowing the contents to drain. As the tank drains under constant agitation, 1 quart of the mixture is taken for every $\frac{1}{10}$-foot interval of depth. This mixture, which is assumed to be a representative sample of the run-off, is placed in a 10-gallon can. The fractional sample for chemical study is obtained from the 10-gallon container by taking $\frac{1}{8}$ pint of the mixture during constant agitation for each $\frac{1}{10}$ foot of water in the storage tank. A special dipper was devised for the purpose. The fraction thus obtained is equal to approximately $\frac{1}{840}$ of the total run-off from the plot.

When water is above the sludge, the procedure is similar to the foregoing except that the contents are not agitated. The number of $\frac{1}{2}$-pint dippers taken is determined by the difference between the measurement of the sludge and the total amount of run-off in the tank. The fraction taken is approximately $\frac{1}{840}$ of the total run-off.

The sludge is weighed in 16-quart buckets. A representative sample is obtained by taking two or more 1-quart samples for each bucket of sludge and placing them in a 10-gallon can. The number of quart dippers taken depends on the total amount of sludge in the silt box. The sample for chemical analysis is obtained from the 10-gallon container by taking four $\frac{1}{8}$-pint dippers for each $\frac{1}{10}$ foot of sludge in the silt box. A more nearly true sample is obtained with $\frac{1}{8}$-pint dippers than with a larger sampler. The fraction thus obtained is equal to approximately $\frac{1}{210}$ of the total plot run-off.

Second and third tanks. All run-off in these tanks is weighed when the total volume of run-off is small. The representative sample is collected in a 10-gallon can by taking a number of $\frac{1}{8}$-pint dippers of run-off from each weighed bucket. When the volume of run-off is large, the tanks are stirred thoroughly and the sample is taken during the draining of the tank. One $\frac{1}{8}$ pint of liquid for each 20 pounds of run-off in the storage tank is taken for the sample for chemical analysis. The fraction collected for the second tank is $\frac{1}{785}$ of the total run-off. The procedure in the third tank is similar to that devised for the second. Because of the additional divisor, the fraction obtained from the third tank represents $\frac{1}{8400}$ of the total run-off.

The approximate volume of the final sample collected from each of the storage

tanks for a storm with one surface-inch of run-off and sent to the laboratory for drying and chemical analysis is as follows: silt box $\frac{22}{64}$ gallon; second tank $1\frac{26}{64}$ gallons; and third tank $\frac{3}{64}$ gallon.

Laboratory procedure

When the field samples reach the laboratory they are evaporated to dryness and stored. No contaminating chemical precipitant is used. At the end of each year the stored samples from each storm are composited from the various tanks in such a manner that the final sample for analysis represents the soil lost from a given plot. In quantity, the stored soil is a fraction of the total soil lost. This fraction already has been indicated. Before analysis, the samples are mixed carefully and ground finely in an agate mortar. Organic matter was obtained from total carbon through the use of the Wolff factor of 1.742.

RESULTS AND DISCUSSION

Data on loss of soil, organic matter, and plant nutrients cover the period from June 12, 1938, to December 31, 1940. During the three growing seasons included in this period, the following crops were grown on all plots: 1938, carrots and beets; 1939, tomatoes; 1940, sweet corn. All crops are planted with the slope, since the objective of the study was to determine the effect of organic matter treatments on soil and water loss. For the purpose of this paper, the effect of slope length on soil losses is disregarded.

There are therefore six replicates for each treatment. Determinations were made on the eroded samples at the end of 1939 and 1940. Hence each value (column 3, tables 3 and 5) represents an average of 24 determinations of the eroded soil. The analyses (column 2) of the plowed layer represent an average of 12 determinations.

The monthly precipitation data at the Marlboro station are given in table 2.

Organic matter losses

A comparison of the percentage of organic matter in the eroded soil with that in the plowed layer for the four treatments is presented in table 3. The factor 4.13 for the check treatment indicates that the eroded material from the check plot contained 4.13 times as much organic matter as was present in the plowed layer. The slightly higher content of organic matter in the plowed layer under the cover crop and manure treatments represents the cumulative effect of organic matter since the treatments were started in 1938. Though the differences are slight, the trend toward higher percentages on the treated plots has been constant. It is not intended to infer that there has been a permanent increase in the organic matter content of the soil, but that there has been a measurable change over the period of investigation. The extent of soil organic matter increase and the duration in the soil of the increased percentage are factors that require additional study.

It is interesting to note that the factors for all four treatments (table 3) are of the same order of magnitude. This indicates, therefore, that the normal process

of erosion removes relatively as much organic matter from the check as from the manure and the cover crop treatments. This is important, for it indicates that additions of organic matter do not increase appreciably the percentage present in the eroded material, and yet at the same time these additions reduce the total soil and water losses.

TABLE 2

Total rainfall, by months, at the Marlboro station for 1938, 1939, and 1940, in comparison with the Freehold, New Jersey, average from 1874 to 1909*

Rainfall in inches

MONTH	AVERAGE RAINFALL FOR FREEHOLD, N. J., 1874–1909	RAINFALL AT THE MARLBORO STATION		
		1938	1939	1940
January	3.96	3.20	3.81	1.90
February	4.02	2.52	4.42	4.12
March	4.65	1.43	5.41	4.11
April	3.64	2.41	4.20	5.30
May	3.84	3.80	0.30	6.50
June	3.63	8.28	2.90	3.00
July	5.12	9.72	1.37	2.13
August	4.71	4.31	6.59	6.11
September	4.29	10.90	1.45	3.07
October	3.52	2.95	2.58	2.61
November	4.02	3.87	3.14	3.90
December	3 72	1.96	0.90	2.44
Total	49.12	55.35	37.07	45.19

* Freehold is approximately 5 miles south of the Marlboro station.

TABLE 3

Comparison of organic matter in eroded soil with that in the plowed layer of Collington sandy loam under various treatments from June 12, 1938, to December 31, 1940

TREATMENT	ORGANIC MATTER IN PLOWED LAYER	ORGANIC MATTER IN ERODED MATERIAL	FACTOR
	per cent	*per cent*	
Check	1.07	4.42	4.13
Cover crop	1.12	5.02	4.48
Manure	1.22	5.16	4.23
Cover crop and manure	1.17	4.64	3.97

The low specific gravity of the organic matter as compared with that of the inorganic fractions probably accounts for the relatively high percentage of organic matter in the eroded material. The organic matter being lighter, it is more easily suspended and then is simply floated off in the run-off.

The percentage of organic matter lost in the eroded material logically must be interpreted on the basis of the total soil lost under the particular agronomic practices. High percentages may be of little or no significance if they are as-

sociated with low soil loss. To provide information on this point, total soil and organic matter losses according to treatments for the period of June 12, 1938, to December 31, 1940, are given in table 4.

The total soil loss indicated in table 4 affords further evidence of the beneficial action of vegetation in reducing soil losses. The rye cover crop, even though affording canopy protection for only 4 or 5 months of the year, illustrates the importance of this protection when compared with the manure plot. The annual application of manure, however, has been effective in reducing soil loss. The initial level of organic matter in the soil undoubtedly was so low that a single application did not increase the infiltration rate for any extended period. With further applications, however, the effectiveness of this treatment on soil losses became more marked, whereas the effect of the rye cover crop has remained fairly constant. The cover crop and manure treatment combined provides the greatest reduction in soil loss. This treatment affords both vegetal protection and incorporated organic matter for improvement of soil structure, aeration, and moisture relations. In addition to conserving soil and water, the organic matter treatments were found to produce larger yields of better quality crops (3).

TABLE 4

Soil and organic matter losses with calculated effective soil loss in terms of organic matter lost from June 12, 1938, to December 31, 1940

TREATMENT	TOTAL ORGANIC MATTER LOSS	TOTAL SOIL LOSS	EFFECTIVE SOIL LOSS
	lbs./A.	*lbs./A.*	*lbs./A.*
Check	1,149	26,000	107,380
Cover crop	609	12,140	54,380
Manure	847	16,420	69,460
Cover crop and manure	337	7,260	28,820

The effective soil loss figures shown in table 4 were obtained by multiplying the actual soil losses by the factors for organic matter loss given in table 3. The calculated effective soil loss indicates the amount of the loss that would be needed to obtain the recorded organic matter loss if erosion from this soil were a uniform process. The results indicate, however, that erosion is highly selective, in that the finer particles and the organic matter are removed more rapidly than the heavier fractions. With a soil having only 17 per cent silt and clay and about 1.25 per cent organic matter, the loss of both the organic matter and the fine soil fractions undoubtedly is one of the major factors contributing to low fertility and impaired moisture conditions.

Plant nutrient losses

Losses of total nitrogen, phosphorus, potash, and calcium were determined for each of the treatments.

Total nitrogen losses are given in table 5. The reduction in total nitrogen losses obtained through the use of a rye cover crop stresses further the econ-

omy of this agronomic practice. The nitrogen conserved by the cover crop, as well as by the cover crop and manure treatment combined, is brought about by two factors; namely, reduction in soil losses and the taking up of nitrogen, which is released later for plant growth when the cover crop is plowed under.

Total phosphorus losses are shown in table 6. The relatively high amount of phosphorus in the plowed layer in comparison with the amount in the lower layers, as shown in table 1, suggests that high phosphorus applications made during the several years of vegetable production have become fixed in the surface soil. Likewise the higher concentration of phosphorus in the surface soil demonstrates again the importance of conservation measures that will prevent the loss of surface soil. The manure treatment alone, as well as the combined manure

TABLE 5

Total nitrogen losses from Collington sandy loam under different treatments from June 12, 1938, to December 31, 1940

TREATMENT	TOTAL N LOST	N IN PLOWED LAYER	N IN ERODED MATERIAL	FACTOR
	lbs./A.	*per cent*	*per cent*	
Check	66.56	.066	.256	3.88
Cover crop	34.72	.070	.286	4.09
Manure	47.13	.067	.287	4.28
Cover crop and manure	19.24	.079	265	3.35

TABLE 6

Total phosphorus losses from Collington sandy loam under different treatments from June 12, 1938, to December 31, 1940

TREATMENT	TOTAL P_2O_5 LOST	P_2O_5 IN PLOWED LAYER	P_2O_5 IN ERODED MATERIAL	FACTOR
	lbs./A.	*per cent*	*per cent*	
Check	153.92	.372	.592	1.59
Cover crop	70.53	.372	.581	1.56
Manure	89.82	.372	.547	1.47
Cover crop and manure	39.71	.372	.547	1.47

and cover crop treatment, was effective in reducing the total amount and percentage of phosphorus lost in the eroded material.

Total potash losses are shown in table 7. The factors for potash (table 7), as well as those for phosphorus and calcium (tables 6 and 8), are lower than the factors for organic matter and nitrogen but are, nevertheless, appreciable. The quantity of potash, phosphorus, and calcium in the eroded material necessarily is related to the percentage of the finer soil fractions removed by the erosion process. This is true because these nutrient elements are relatively most abundant in the finer soil fractions, which are in turn most subject to erosion.

Total calcium losses are given in table 8. In an attempt to adjust the pH of all plots to approximately 6.5, it was necessary to make applications of limestone,

ranging from 3,000 to 5,000 pounds to all the plots, during 1938 and 1939. The limestone was broadcast and worked into the soil. The amount of calcium present in the soil profile (table 1) appears to be fairly constant throughout the various horizons. The large losses of calcium suggest that erosion is one of the important factors responsible for the increase in acidity that takes place in this soil when under cultivation.

TABLE 7

Total potash losses from Collington sandy loam under different treatments from June 12, 1938, to December 31, 1940

TREATMENT	TOTAL K_2O LOST	K_2O IN PLOWED LAYER	K_2O IN ERODED MATERIAL	FACTOR
	lbs./A.	*per cent*	*per cent*	
Check	514.80	1.36	1.98	1.46
Cover crop	230.66	1.36	1.90	1.40
Manure	310.34	1.36	1.89	1.39
Cover crop and manure	117.61	1.36	1.62	1.19

TABLE 8

Total calcium losses from Collington sandy loam under different treatments from June 12, 1938, to December 31, 1940

TREATMENT	TOTAL CaO LOST	CaO IN PLOWED LAYER	CaO IN ERODED MATERIAL	FACTOR
	lbs./A.	*per cent*	*per cent*	
Check	141.18	.263	.543	2.06
Cover crop	79.76	.263	.657	2.50
Manure	101.31	.263	.617	2.35
Cover crop and manure	34.96	.263	.633	2.41

SUMMARY AND CONCLUSIONS

Erosion losses of organic matter and major plant nutrients are reported for Collington sandy loam used for vegetable production under New Jersey Coastal Plain conditions. The field technique employed in obtaining fractional samples of the actual run-off material is described.

Losses of soil, organic matter, and plant nutrients were reduced by the use of a rye cover crop, as well as by the application of 20 tons of manure annually. A combined treatment, consisting of a rye cover crop plus 20 tons of manure, had a marked effect on soil and water losses.

Losses of organic matter and plant nutrients from the check plots, which lost 26,000 pounds of soil from June 12, 1938, to December 31, 1940, were as follows: 1,149 pounds of organic matter, 67 pounds of nitrogen, 154 pounds of phosphoric acid, 515 pounds of potassium oxide, and 141 pounds of calcium oxide. An application of 20 tons of manure per acre each year combined with a rye cover crop reduced soil losses to 7,260 pounds, with other losses as follows: 337 pounds organic matter, 19 pounds nitrogen, 40 pounds phosphoric acid, 118 pounds po-

tassium oxide, and 35 pounds of calcium oxide per acre. Average losses of organic matter and plant nutrients from the four treatments showed that 4.20 times as much organic matter, 3.90 times as much nitrogen, 1.52 times as much phosphoric acid, 1.38 times as much potassium oxide, and 2.33 times as much calcium oxide were lost in the eroded material as were present in the plowed layer of Collington sandy loam.

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EFFECT OF SUBMERGENCE ON A PODZOL SOIL PROFILE IN THE ADIRONDACK FOREST

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A study by Donahue[2] shows that in the central Adirondacks the spruce-hardwood and spruce flat types of forest are associated with a strongly podzolized soil profile, whereas the northern hardwood type is associated with the less podzolized brown podzolic soil group. The spruce flat forest consists mainly of red or black spruce and balsam fir; the spruce-hardwood type contains red spruce, hemlock, and a mixture of hardwoods, especially yellow birch, beech, and sugar maple; the northern hardwood type is without conifers except for an occasional hemlock or red spruce, and the better hardwoods, as white ash and basswood, may be present.

A typical podzol profile, such as occurs under spruce-hardwood or spruce flat forests, shows the following features (physical and chemical data omitted): Beneath the leaf litter is an A_0 horizon (H-layer) from 2 to more than 8 inches deep, consisting of finely divided organic matter usually permeated by roots; commonly this humus layer constitutes a granular or greasy mor.[3] Below this comes an abrupt change to mineral soil, the first layer of which (the A_2 horizon) is grayish white, 1 to 5 inches deep, with almost no organic matter; the appearance of this horizon is due, in part at least, to the leaching out of organic matter and of iron and aluminum compounds. Next comes a series of two or three B horizons, in which these leached materials have been redeposited in varying amounts. The B_1 horizon is dark brown or black, 1 or 2 inches deep, and the B_2 and B_3 horizons (not always clearly separable) extend down some 10 to 18 inches farther, changing from reddish brown to very pale brown before meeting the wholly inorganic C horizon.

From the nature of a soil profile in this region, then, it is possible to infer something of the nature of the forest, and conversely, from the type of forest one may deduce (except in transitional areas) something of the degree of podzolization of the soil profile. The occurrence of a typical podzol profile in an area which had been cleared of all timber and then flooded for 15 years is therefore of some interest, showing a resistance to change in spite of this interference with the normal processes of drainage and leaching, and also showing other special effects of submergence.

[1] For the suggestion which led to this study the writer is indebted to Ralph T. King, director of the Roosevelt Wildlife Forest Experiment Station and of the Huntington Wildlife Forest Preserve.

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Adjidaumo Lake, locally called "The Big Flow," is in the Huntington Wildlife Forest Preserve, Newcomb, New York. A shallow artificial reservoir about 0.7 mile long and 0.4 mile wide, it was produced about 1912 by damming, in order to provide water for carrying logs. The following paragraph is quoted, by permission, from a letter by O. W. Oja, Supervisor of the Huntington Forest, dated December 8, 1941:

> The softwood logging in the section occurred about 45 years ago. In 1910–11, it is reported that one Clinton Simonds surveyed the area which would be flooded by the wooden dam which was installed the following year or so. The area that was flooded was first cleared of all timber about 1911–12. About 1926–28 the wooden dam failed and much of the water went out. The last of the water was let out in 1939, when the CCC removed the debris which had formerly been the dam.

Sedges and grasses now grow over much of the area, among water-worn stumps of the original forest. On November 19, 1941, the writer accompanied Frank B. Barick, biologist in residence at the Huntington Forest, in an examination of

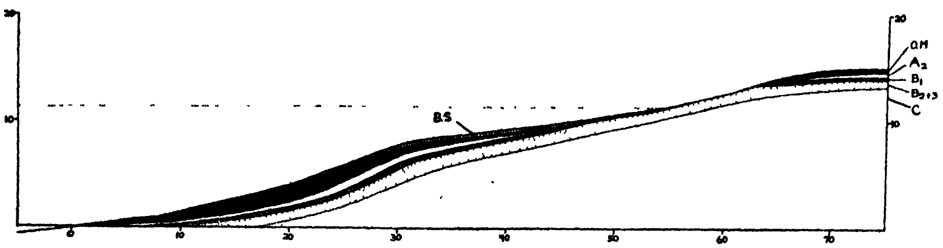

FIG. 1. DIAGRAM OF A PODZOL PROFILE BELOW FORMER LAKE ADJIDAUMO
Distances and heights, in feet. Original water level of lake indicated by dotted line. O. M., organic matter; B. S., coarse sand

the lake bottom and shore line. A trench and series of pits dug from the present stream level to the present spruce-hardwood forest bordering the tract showed a podzol profile below the former lake, continuous, except for erosion at the beach-line, with that of the unaffected forest.

THE PODZOL PROFILE

Figure 1 is a diagram of this profile. The distances and heights are in feet. The location is the narrower part of the lake bed about 200 yards above the outlet. Release of the lake water caused a drop, at this point, of about 11 feet and a lateral recession of some 55 feet. Boulders and stumps are numerous, but are not shown in the diagram.

In the lower part, the surface layer is of incompletely decomposed wood fragments and sedge deposit, black and loose. Three feet from the edge of the present stream this organic layer is 4 inches deep; 10 feet from the edge, 12 inches deep; and 20 feet from the edge, 18 to 20 inches deep. The deeper part is blacker, finer, and more compact than that toward the surface; the latter, except for a small amount of sedge deposit, is fragmentary wood which covered most of

the bottom of the lake. At 30 feet from the water the organic layer is reduced to a thickness of only 3 or 4 inches, is wholly of the fine, compact material, and is covered by 2 or 3 inches of coarse sand. It is absent in a zone extending from 45 to about 65 feet from the water, and appears again in the spruce-hardwood forest as a granular mor humus layer 2 inches deep, beneath litter and moss. The usual podzol profile occurs in this forest.

The coarse sand appears to have been derived by wave action from the boulders and pebbles (anorthosite, quartzite, calcite of the Grenville formation, and granite) at the former shore line. The sand spreads from there down to about 25 feet from the present water edge. It has mingled only to a slight degree with the organic layer which it covers.

A leached layer (A_2) extends continuously beneath the organic layer from the water line to the upper limit of the organic deposit, and again beneath the humus layer in the forest. It varies from 1 to 3 inches in depth, being deepest about 20 to 30 feet from the water. Where it reaches the stream level and is submerged permanently it becomes barely distinguishable from the mineral soil below, being pale gray, whereas the latter is brownish gray.

Ten feet from the water there is still no distinct B_1 or B_2 horizon, but both B horizons are clear at 20 feet. The upper part of the B series, including the dark-brown B_1 (1 inch) and the reddish-brown B_2, is compacted into a typical ortstein, which resists the spade but may be broken into large lumps. The depth of this is 4 to 6 inches, below which the B horizon shades into the greenish-yellow-brown C horizon.

The organic layer, the A_2 horizon, and the B_1 horizon are discontinuous at the beach level, but the reddish B_2 extends the entire distance from the lower slope to the spruce-hardwood forest, without, however, any ortstein beyond 40 or 45 feet.

CONCLUSIONS

Certain inferences are now possible. The most obvious effect of submergence upon this podzol profile is the erosion of the upper part in the zone of wave action. Another effect is the burial of a broad part under coarse beach sand derived largely from projecting boulders. The depth and the loose, coarse nature of the organic layer in the formerly submerged part is due to accumulation of rotting wood on top of the original humus layer (granular or greasy mor) present before the lake was formed. The latter probably persists as the fine, compact material just above the A_2 horizon. The relative shallowness of the organic layer close to the present water level may be due to some small wave and stream activity, carrying away the looser fragments since the bulk of the water went out. At the level of the permanent water table the distinction between horizons underneath the organic layer virtually disappears. Presumably the podzol profile had little opportunity to develop here on account of the lack of drainage even before the lake was made.

At the time of these observations the writer took samples for study of the soil fauna (arthropods and annelids) at certain points along this transect, and for broad comparison with the fauna already found in humus layers at other sites in

the Adirondack forest. As only one sample was taken at each point, the figures cannot be used as reliable population counts, but they clearly show the gross effect of the changed conditions upon the fauna. Each sample was taken by removing 0.2 square foot of material to a depth of 1 inch. The sample was dried slowly in a modified Berlese funnel, which extracted approximately the whole arthropod and annelid fauna. The locations were as follows: I, 3 feet from stream edge, at surface; II, 20 feet from stream edge, at surface; III, 20 feet from stream edge, at depth of 12–15 inches; IV, 75 feet from stream edge, in the spruce-hardwood forest, under moss and spruce litter, at surface. The following results show number of individuals per square foot 1 inch deep:

SAMPLE	I	II	III	IV
Enchytraeid worms	58	...	...	..
Mites	108	72	...	3780
Pauropods	9	5	...	..
Collembola (springtails)	163	5	...	81
Beetle larvae	.	...	...	36
Fly larvae	50	22	...	9
Total	388	104	...	3906

It is clear that in the exposed lake bed, in spite of a high organic and moisture content, the animal population is scanty, and that it does not extend to the deeper part of the organic layer (sample III). Previous work of the author has shown that the population is greatest at the level where the leaf litter is being broken down to form the humus layer, and that it gradually declines, although animals are still present in substantial numbers, through the whole of a granular or greasy mor humus layer in the spruce-hardwood or spruce flat type of forest. For example, the following figures were obtained as an average of two granular mor humus layer sites (spruce-hardwood forest) in another part of the Huntington Forest; each figure represents, as before, the population of a square foot area 1 inch deep:

ANIMALS	LITTER AND F LAYER	UPPER PART OF HUMUS LAYER	LOWER PART OF HUMUS LAYER
Mites	3340	825	325
Springtails	670	365	110
Other arthropods and potworms	105	45	10
Total	4115	1235	445

Returning to the Adjidaumo Lake site, the count of mites in sample IV, from the unaffected forest, agrees well with the average given here; the count of other forms is lower, but this may be due to a covering of moss over most of the surface. The large number of potworms (enchytraeids) in the sample closest to the water

may be due to high water and organic content, but such forms are generally common in humus layers.

During the time of submergence, none of the animals noted here, except possibly the potworms, could have lived in the lake bottom. The fauna has therefore invaded the lake bed since its exposure, and while showing little influence so far upon the structure or composition of the organic layer, may be expected to increase with the coming of more vegetation and eventually help to reduce this layer to a finely divided material resembling granular or greasy mor.

SOME EFFECTS OF BLACK LOCUSTS AND BLACK WALNUTS ON SOUTHEASTERN OHIO PASTURES[1]

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"There is but one tree which will, to my knowledge, benefit the pasture land as pasture, and that is the black locust, which, being a legume, enriches the soil," wrote Joseph E. Wing[3] in 1912 (13). This opinion has been widely held, but it is not accepted by all observers. Some have claimed that trees of any type are detrimental to pastures, whereas others believe that black walnuts as well as black locusts lead to pasture improvement.

In addition to these opinions based upon observation alone, there is considerable information from investigations dealing with special phases of the problem. Chapman (2) attributed the superior growth of orchard grass that he remarked under black locusts to the nitrogen supplied by the trees. Gustafson (4) suggested, as a result of certain observations and litter measurements under black locusts on sandy areas, that the favorable effect of the trees upon the bluegrass could be explained by the nitrogen and other nutrients supplied, the moisture held, and the temperature reduction by the locust leaves. Graman and Merkle (3) found evidence of increases of mineral nutrients in the soil under locusts. In connection with observations of beneficial effects of, black locusts and black walnuts upon West Virginia pastures, Broadfoot and Pierre (1) studied rates of leaf decomposition in the laboratory and correlated their results with certain chemical properties of the leaf samples. The leaves of these two species were found to decompose more rapidly and to contain more basic materials than most of the other leaf types studied.

An experiment to determine quantitatively whether black locusts and black walnuts actually do improve pasture herbage was established at the Middle Tennessee Agricultural Experiment Station in 1926. The results reported by Neel (6) indicate distinct improvement in the carrying capacity of both the

[1] This investigation was made possible by the joint support of the Ohio Agricultural Experiment Station and the Hillculture Division of the Soil Conservation Service. A more detailed account of the methods and results is contained in a dissertation submitted to the Ohio State University in partial fulfillment of the requirements for the degree of doctor of philosophy.

The author is indebted for advice and assistance to many representatives of the Ohio Agricultural Experiment Station, the Ohio State University Agronomy Department, and the Soil Conservation Service; and especially to L. D. Baver, of the North Carolina State College, and to O. D. Diller, of the Ohio Agricultural Experiment Station, under whose supervision the study was conducted.

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[3] Joseph E. Wing is especially remembered as an early proponent of the value of alfalfa and alfalfa-grass mixtures in the eastern corn belt.

locust and the walnut plots compared to the open check plots. The greater advantage was from the locusts. Improvement was evident both in the amount of Kentucky bluegrass on the plots and in the pounds of beef produced.

The present study represents one phase of the Hillculture research program for Ohio. The purpose has been to measure some effects of black locusts and black walnuts and other trees upon the forage covers of southeastern Ohio pastures; and, through consideration of the various interrelated factors, to arrive at some basis for making predictions and practical suggestions for pasture improvement and for further research.

SITE SELECTION

In choosing tree-covered grass areas for study in comparison with open pastures, care was taken to eliminate insofar as possible all variables other than the presence of the trees. This necessitated the restriction of sites to relatively level areas where erosion was not active, for it was found that on sloping erodible land the greater depth of surface soil and the retarded runoff under the trees might be sufficient to account for great differences in the vegetation. For instance, on slopes ranging from 10 to 25 per cent, the average depth of surface soil under 23 isolated trees measured 11 inches as compared to $4\frac{1}{2}$ inches on the adjacent open areas. The maximum depth was 19 inches under the trees and 8 inches on the open slopes, and the minima were 6 and 0 inches, respectively. All of these sites were excluded.

Trees in fence rows, and those under which animals were likely to congregate were also eliminated, as were others where tillage differences were evident or seemed likely.

The sites selected were scattered but were all within a radius of approximately 15 miles of the Senecaville Dam in Guernsey County, Ohio.

The soils represented were derived from residual material: from limestone, from sandstone, and from shale. Limestone is more abundant in this area than throughout the Appalachian plateau region in general, but not all sites studied showed indications of limestone contributions, and at only a few was limestone the main source of the soil material. Most of the sites would be classified in the Westmoreland soil complex. Several belong in the Muskingum soil series.

HERBAGE YIELDS

Throughout the 1939 and 1940 seasons, yields of herbage were obtained from 4- by 4-foot plots under black locusts and black walnuts and from paired adjacent plots in the open pasture just beyond the influence of the tree. The plots not under the influence of trees are referred to in this paper as *check plots*.

Since each pair of plots was chosen to represent a particular situation, the logical procedure would be to consider each comparison individually as to species, density, yield, composition, and root development of the ground covers, and to relate these characteristics to the local conditions for growth. As, obviously, it is not practical to resort to such a detailed presentation, the yields are sum-

marized (table 1) to give a general idea of the results, and some of the individual circumstances and relationships essential to a proper interpretation are brought out in the discussion and the additional information that follows.

The species contributing to the yields at the different sites were very different. In no case were they distinctly more desirable on the check plot than on the plot under the trees; in most cases, in fact, the reverse was true. The main undesirable grass under trees was nimblewill (*Muhlenbergia shreberi*), which usually does not perist under heavy grazing. On all check plots that gave higher total yields than the walnut plots, the main grass was broomsedge (*Andropogon virginicus*).

There were more weeds, on the average, on the check plots; therefore the total yields would have been more favorable to the checks if weeds had not been dis-

TABLE 1

Comparison of herbage and protein yields under trees with yields from check plots

Average yields per acre

PLOTS	NUMBER OF PLOTS		TAME GRASS AND CLOVER*	DRY WEIGHT YIELD†		NUMBER OF DRY WEIGHT YIELDS FAVORING TREE PLOTS		PROTEIN IN HERBAGE		
	1939	1940		1939	1940	1939	1940	1939	1939	1940
			per cent	*lbs*	*lbs*			*per cent*	*lbs*	*per cent*‡
Under walnuts	14	12	67	1,621	1,710	11	10	13.7	211	11.0
Checks	14	12	31	1,151	1,285			12.1	135	9.5
Under locusts	9	9	70	1,263	1,754	7	4	18.6	227	16.3
Checks	9	9	29	1,021	1,719			13.5	132	10.5

* From vegetation counts by the inclined "point quadrat" method.

† Note that these yields are low. This is due in part to the fact that the pastures are not highly productive; but it should be kept in mind that summer rainfall was below average in 1939, and rainfall was so distributed in 1940 that pasture yields were probably not above average.

‡ Incomplete analyses.

carded. The elimination of some weeds by clipping is, doubtless, a factor contributing to the increased yields on the check plots in 1940 over those in 1939.

An important consideration in connection with these yields is their seasonal distribution. In the denser locust groves (fig. 1), almost all the growth had occurred by the first of June. Where the locust stands were thin and the trees were trimmed to a height of 10 to 12 feet (fig. 2), the seasonal distribution was similar to that of the open pasture, except that under all locusts, growth started a few days earlier in the spring. In some places, grass under black walnuts continued growth somewhat longer in midsummer than did grass in the open. Otherwise, the seasonal distribution was similar to that of the open pasture.

Grass that grows early in the season in dense locust groves remains green and immature throughout the summer. This is true also to some extent of grass under open stands of both locusts and walnuts.

FIG 1. GRASS UNDER DENSE GROVE OF BLACK LOCUSTS STUDIED IN COMPARISON WITH OPEN PASTURE

This locust stand is too dense for much forage production except very early in the season. The grass under the trees is mainly Canada bluegrass. Dry weight yields were higher on the check plot (foreground). The grass under the locusts was much higher in protein.

FIG 2. GRASS UNDER THIN STAND OF BLACK LOCUSTS STUDIED IN COMPARISON WITH OPEN PASTURE

Note the denser ground cover and the absence of broomsedge under the trees. The grass under the trees is mainly Kentucky bluegrass; that in the open, wild grasses and weeds. The yield of herbage under the trees was much superior to that in the open, both in 1939 and 1940

FIG. 3

FIG. 4

FIG. 3. UNMISTAKABLE EVIDENCE OF GRAZING UNDER A BLACK WALNUT TREE

Note the height of the ungrazed grass outside the fence. Note also the density and uniformity of the Kentucky bluegrass cover under the tree and the characteristic scarcity of walnut litter.

FIG. 4. CLOSEUP OF BLACK WALNUT ROOT SYSTEM

Note the absence of walnut roots from the upper few inches of soil, the density of the Kentucky bluegrass, and the scarcity of walnut litter.

HERBAGE COMPOSITION

Nitrogen

The harvests of 1939 were analyzed for nitrogen by a modified Kjeldahl method. The results, calculated to protein, are summarized in table 2. All the plots under locusts yielded more protein than the corresponding check plots (see also table 1). The high protein values in the herbage under the locusts were very consistent, evidently reflecting the nitrogen supplied by the trees, for there was somewhat less clover under the trees than in the open. Only one check sample at one harvest was higher in protein than the corresponding locust sample. The small differences in favor of the grass under the walnuts would be expected as a result of shade.

Selected samples of forage from the 1940 harvests were analyzed for nitrogen, which again was calculated to protein (table 1). The results were somewhat similar to those of the complete analyses for 1939.

TABLE 2

Protein, calcium, and phosphorus in oven-dried herbage under trees and from check plots

Averages for 1939

HARVEST	PROTEIN		CALCIUM		PHOSPHORUS	
	Under walnuts	Checks	Under walnuts	Checks	Under walnuts	Checks
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
First	12.3	11.6	0.34	0.31	0.18	0.16
Second	14.9	14.4	0.45	0.37	0.20	0.16
Third	14.1	11.2	0.42	0.35	0.21	0.18
	Under locusts	Checks	Under locusts	Checks	Under locusts	Checks
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
First	16.6	12.6	0.34	0.40	0.18	0.16
Second	20.0	15.6	0.50	0.61	0.20	0.19
Third	19.2	12.5	0.45	0.55	0.20	0.18

The fact that high protein percentages were found in the grass under the most widely spaced locusts suggests that a sufficient supply of nitrogen for the grass does not require a close spacing of the trees. The results even suggest that the check plots near locusts were receiving some benefit from the nitrogen from the trees. Otherwise the grass under the walnuts would be expected to be distinctly higher in protein than that on the check plots near locusts, because of the factors of shade, of more desirable species, and of better soil condition under the walnuts.

It is possible that the grass on some of the check plots was influenced by nitrogen from the locusts, because roots from the trees were found very close to several of these plots.

Calcium and phosphorus

The herbage harvested in 1939 was analyzed for calcium by the standard oxalate-permanganate method, and for phosphorus by the method of Zinzadze

(14). Samples were prepared by wet digestion with nitric and perchloric acid. The results are summarized in table 2.

Interpretation of these analyses is complicated by the fact that various grass and clover species were involved. Even so, the higher percentage of phosphorus under the trees was consistent in all but a few cases, as were the results with calcium under the walnuts. The exceptions seemed related to clover on the check plots. On the other hand, the calcium values involving locusts were not consistent, the higher averages on the check plots being due to a few very high values. These were obtained on plots with some clover, in comparison with plots of Canada bluegrass in the denser locust groves.

In general, the conclusion may be drawn that where grasses alone are considered, both calcium and phosphorus will be somewhat higher under thin stands of trees than in the open, but, if the trees eliminate clovers, they are likely to lead to lower contents of both these elements. The higher percentages and higher total yields of phosphorus in grasses under the trees raises the question as to whether better phosphorus nutrition may be involved in the beneficial effects of trees in some cases.

SPECIES AND DENSITY OF HERBAGE

The inclined "point quadrat" method of Tinney et al. (9) was used to study the distribution of ground cover plants and their density. Counts were made at most sites in the spring of 1939 and again in the late summer of 1940. The counts were used to compare the vegetation under certain tree species with that on adjacent check areas and with that under other tree species. The vegetation counts were continually supplemented by observations throughout the 2 years of the study. A detailed interpretation of the information obtained would require a consideration of the conditions of each individual site, but a generalized picture may be outlined as follows:

Trees of any type in southeastern Ohio pastures usually introduce differences in the ground cover species and density compared to the open pasture. The differences vary with the type and spacing of the trees.

Under thin stands of black walnuts and black locusts (fig. 2), the density of the forage covers is comparable to that of open bluegrass pastures. The dominant species in such situations is usually Kentucky bluegrass. Other grasses commonly found include nimblewill, timothy, redtop, and meadow fescue. Nimblewill usually occurs as a minor species in Kentucky bluegrass sods; meadow fescue is the dominant grass when it occurs; and timothy and redtop occur in mixtures.

Under black locusts in groves (fig. 1) and under many maples, beeches, oaks, and hickories, Canada bluegrass is the dominant forage species, but it rarely occurs under black walnuts, even in dense stands. The Canada bluegrass cover in the situation described is usually thin.

Poverty oat-grass (*Danthonia spicata*) and various "poverty" weeds frequently are found under maples, beeches, oaks, and hickories, but rarely under black walnuts or black locusts, even on poor sites.

Broomsedge rarely is found under trees of any type.

Pastures with poverty grass or other poor ground covers are almost certain to profit as to species and density from the presence of scattered black locusts or black walnuts.

Productive Kentucky bluegrass pastures are almost certain to suffer, both as to species

and density, from the presence of maples, oaks, beeches, and hickories. There would be little effect from widely spaced black walnuts and probably no great effect from widely spaced black locusts.

ROOTS AND RHIZOMES OF HERBAGE

The most consistently evident characteristic of the underground grass parts in this study was the shallowness of roots and rhizomes under black locusts in groves. This seemed to be associated with increasing proportions of Canada bluegrass under the trees. The same characteristic of the rhizomes of Canada bluegrass was reported by Watkins et al. (11).

Although the most shallow roots and rhizomes observed have been from Canada bluegrass, it has seemed that Kentucky bluegrass, even in thin groves of black locusts (20-year-old trees spaced at 15 to 20 feet), lacks the root depth common to that grass in the open. But under individual locust trees or under black walnuts, the underground parts of the grass are apparently as deep as in the open pasture.

The total quantity of grass roots and rhizomes is evidently related to the depth of root development. Soil samples taken under black walnuts contained slightly more grass parts than samples taken in the open, and samples under locusts contained slightly less. The smallest quantities were obtained in the densest locust groves.

HERBAGE PALATABILITY

It has not been possible to establish any positive basis for measuring relative palatability in this study, but repeated observations have shown that grasses under black locusts and black walnuts are eaten readily by livestock, (fig. 3) and actually are preferred under some conditions.

The following factors seem to favor the apparent palatability of pasture under trees at certain seasons: more palatable grass species, shade protection for the animals, more moisture in grasses (during dry summer seasons), and delayed maturity of grasses.

There are also factors that may favor the apparent palatability of open pasture: more white clover, more sugar in herbage [mainly in contrast to dense shade (12)], and less moisture in grass (during moist spring seasons).

SOIL TESTS

Differences in the soil under black locusts and black walnuts have been found confined largely to the surface 3 inches. All comparisons were between carefully paired samples where the only basic difference was the presence of the tree. No surface litter was included in the samples. If proper precautions against differences in erosion, animal manure, and tillage are not taken in sampling, much more striking results are likely to be obtained. A general summary of the tests of 0- to 3-inch samples is given in table 3. Soluble phosphorus determinations also were made, but they showed no significant differences.

Organic matter was determined by a chromate oxidation method modified from Schollenberger (8); pH with the glass electrode; exchangeable bases by the

Kappen equilibrium method (5). Phosphorus was extracted by the method of Truog (10), and determined by that of Zinzadze (14).

The pH and exchangeable base differences under locusts are not consistent enough to be clearly significant. The other differences shown are significant, and, although not great, are sufficient to influence the growth of herbage. The organic matter content of soil under trees undoubtedly reflects to some extent the cooler microclimate, as well as the supplies of organic materials (table 3).

TABLE 3

Summary of soil tests under trees compared to check areas

0- to 3-inch soil samples

	UNDER TREE	CHECK	NUMBER OF COMPARISONS	NUMBER FAVORING TREE SAMPLES
Black walnut comparisons				
Organic carbon ... *per cent*	3.0	2.2	37	34 (1 even)
pH ...	6.2	5.9	40	36
Exchangeable bases ... *m.e./100 gm.*	16.1	11.5	32	29
Volume weight ...	0.95	1.09	16	15 lower
Black locust comparisons				
Organic carbon ... *per cent*	2.1	1.6	18	16
pH ...	5.5	5.3	18	9 (5 even)
Exchangeable bases ... *m.e./100 gm.*	9.9	7.9	13	8
Volume weight ...	1.13	1.19	10	6 lower (1 even)

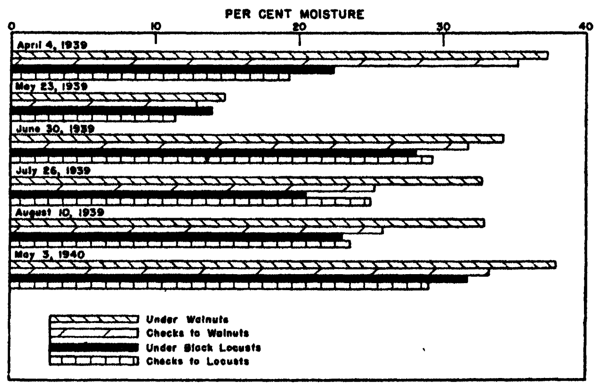

FIG. 5. MOISTURE IN SOIL UNDER TREES COMPARED WITH THAT IN SOIL ON ADJACENT CHECK PLOTS

Averages of 0- to 3-inch samples on several dates

Volume-weight determinations have indicated a less dense soil under black walnuts and under widely spaced black locusts than in open pastures, and observational studies have indicated better granulation. Earthworms have seemed especially active under walnuts, where their effect upon stable aggregation has been very marked.

Soil-moisture determinations were made by oven-drying samples from a number of sites on various dates. Not all of the comparisons gave consistent results, but certain general relationships seem clear (fig. 5). The dates included are those on which the largest numbers of samples were taken. Not all of the same sites were represented on every date.

The surface 3 inches of soil under the trees averaged higher in moisture, except under locusts in the summer (fig. 5). The driest sites in summer were in the dense locust groves. Soil-moisture equivalents determined were not sufficiently higher under the trees to indicate that the relationships would be different in terms of available moisture. Samples below 3 inches have indicated generally less moisture under trees in summer. Samples under maples and other shallow-

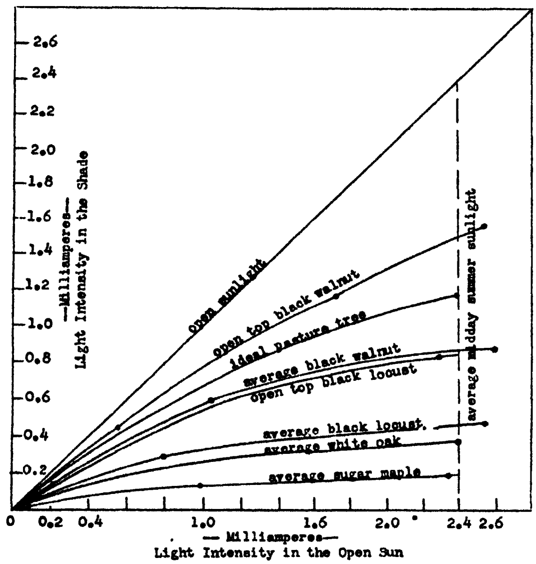

FIG. 6. RELATIVE LIGHT INTENSITIES UNDER DIFFERENT TREE SPECIES

Individual trees, except *average black locust*, which refers to pastured groves as they occur

feeding trees have indicated that the surface 3 inches is frequently very dry in summer.

LIGHT INTENSITY

The most marked vegetation differences under trees in some places are extended north or east, suggesting shade as their primary cause. Such is the case in the occurrence of Kentucky bluegrass under many trees farther south. In Ohio this extension north or east is sometimes evident, but more frequently it is not. This is not an indication that shade is an unimportant factor in Ohio; it merely serves to emphasize the importance of other factors as well.

The light intensity under various trees was measured with a Photronic cell and milliameter in the early summer of 1940. Some of the relationships determined are summarized in figure 6.

Black walnuts on the average cast less shade than any other common tree of the area. Isolated black locusts cast less shade than many other common trees, including most oaks and hickories. Individual walnuts cast denser shade than some locusts. Sugar maples cast the densest shade measured.

TREE LITTER

Because of the rapid rate of disintegration and decomposition of the tree litter very little accumulates under black walnuts or widely scattered black locusts. In locust groves several tons of litter may accumulate per acre, but the amount is not so great as under most forest trees. Black-walnut litter breaks down somewhat more rapidly than that of black locust. This rapid breakdown probably accounts for the belief that walnut litter usually blows away; actually, more of it remains than under most other trees, for it works into the grass and is held in spite of the wind.

Amounts of certain nutrients equivalent to the following may be added annually to the surface soil in the litter from isolated walnuts and locusts: $CaCO_3$, 100 to 150 pounds per acre; P_2O_5, 5 to 7 pounds; nitrogen, 20 to 35 pounds. These values are based upon an estimated annual litter fall of 1,500 pounds of dry matter per acre, and a number of analyses of litter collected immediately after it had fallen from the trees in 1939.

The fact that there is an appreciable build-up of bases in the surface soil under walnuts from the relatively small annual contribution of the litter indicates that the combination of walnuts and grass is a very efficient system. The minerals used by the trees are probably derived mainly from soil horizons below the layer occupied by grass roots. Leaching losses probably are slight.

It is probable that the difference in favor of the soil under walnuts compared to checks is less in heavily grazed than in lightly grazed areas. This does not detract from the desirability of the walnut-grass combination, for it probably means that the annual removal of forage and of bases has been higher under the trees than in the open pasture. Many of the comparisons made were in lightly grazed areas.

The nuts produced by walnut trees are undoubtedly a factor in the nutrition of the grass in some places, but since only a few of the trees in this area produce nuts regularly and many of them produce no nuts at all, this possible contribution need not be given primary consideration. Observations have indicated that the nuts under walnut trees have essentially the same effect upon grass as does the litter. The discussion of the effects of litter may be considered to include nuts, when these are present.

The effect of tree litter upon grass growth seems worthy of more consideration than it commonly receives, but evaluation of its importance is difficult. Certainly its effects are both physical and chemical, and may be either detrimental or beneficial, depending upon the type of litter and the type of ground cover. Black-walnut litter apparently approaches the ideal for Kentucky bluegrass. It forms a very fine light mulch without smothering the grass. Then it readily works into the soil and undergoes rapid decomposition with resultant release of its nutrient content.

But even so, observations in the early spring have suggested strongly that the grass under black walnuts may be severely stunted by lack of nitrogen. This would result from the incomplete decomposition of the carbonaceous litter to a favorable C-N ratio (7). The same type of stunting has been noted under other trees with more resistant leaf types but has never been seen under black locusts, even though more carbonaceous litter was present than under walnuts. Further evidence is supplied by the observed vigor of grass growth around dead trees, where decomposition of the carbonaceous matter has been more complete.

Accordingly, it is suggested that nitrogen starvation may be responsible in part for the poor grass growth under many trees and may play an important role in the elimination of certain species, such as Kentucky bluegrass. Under many black walnuts the relatively low yields made by pure stands of Kentucky bluegrass probably result from a lack of available nitrogen.

Winter grazing favors the rapid decomposition of leaf litter, and observations have suggested that this favors the next year's growth of grass. Thus, it seems that management may be an important factor in tree-covered pastures.

TREE ROOTS

The natural distribution of tree roots in the soil was given considerable attention in this study. No common tree species in the area seemed to have fewer feeding roots in the shallow surface soil than the black walnut, and most species had many more. A characteristic walnut root system is shown in figure 4. The large branch roots, in some instances, are closer to the surface, but in such cases most of the smaller branches turn downward into the soil rather than upward into the zone of the grass roots.

Black locusts have more surface feeding roots than walnuts, but not so many as beeches or maples. There are more shallow tree roots in black locust groves than under isolated trees.

PERIOD OF TREE ACTIVITY

Observations both in 1939 and 1940 have revealed that black-walnut leaves start to develop later in the spring and more of them are lost during the summer and early fall than is characteristic of other common trees. The leaves do not reach full development until nearly the first of June. This may be an important factor in the superior growth of grass under walnuts, for there is extra opportunity for the grass to grow in the spring before the leaves develop, and in the fall after they have been shed.

GENERAL DISCUSSION AND CONCLUSIONS

Interpretation of the results obtained depends to some extent upon the individual point of view and the criteria used for the measurement of pasture improvement; but from any point of view it seems clear that under certain circumstances there is a beneficial effect upon pastures from the presence of widely spaced black walnuts and black locusts, in addition to the influence of these trees through prevention of erosion.

In extremely poor pastures of southeastern Ohio, trees of almost any species

are likely to be of some benefit. On the other hand, in highly productive white-clover-Kentucky-bluegrass pastures there is little reason to believe that improvement could ever be accomplished by trees of any type, and there is abundant evidence that most trees would cause considerable injury.

On the ordinary pasture, which is not very productive in this area, the introduction of widely spaced black walnuts or black locusts certainly would cause no injury, and in many cases, would improve the forage, whether measured in species, yields, composition, palatability, or seasonal distribution.

It is not possible to say how high the level of production under trees could be raised by the use of fertilizer and other means. Wide spacing of the trees and trimming of the lower branches certainly would be required as other limiting factors were corrected, but there is no indication that yields could not be increased with fertilizers, as long as the trees were spaced to prevent overlapping of their branches.

The most serious detrimental effect likely to be encountered in actual practice is the elimination of white clover by the trees. There was not enough clover involved in the studies made to indicate how completely this would occur, but there was an indication that the tendency would be in that direction, especially with black locusts. Nitrogen supplied through the locusts, however, might offset the loss. In the only case where a check plot with a high proportion of white clover was compared to a pure stand of Kentucky bluegrass under locusts, the pure Kentucky bluegrass was higher in nitrogen and gave a higher total yield of nitrogen than the mixture of bluegrass and white clover in the open. The locusts in this comparison were spaced near the optimum for pasture. It would be interesting to know what would have been the result if both plots had received liberal applications of phosphate and potash fertilizers.

The effect of trees upon pasture grasses cannot be considered as a simple phenomenon with a single cause. Rather, it represents the net effect of the alterations introduced by the tree, that is, the reduced light, the tree leaf fall, the tree root competition with the grass and with weeds, and the many indirect reactions of these factors through soil condition, soil moisture, soil temperature, and soil organisms. Whether this net effect is beneficial or detrimental depends upon the type of pasture, the type of soil, the climate, and the season, as well as upon the type of tree. A clearer understanding of the factors involved is essential to accuracy in the prediction of results.

The importance of this concept of the net effect is well illustrated by the black locust. The need of poor pastures for nitrogen seems readily satisfied by this tree, but there are many questions concerning the extent to which this nitrogen can be utilized without serious limitations to growth from the tree root competition or from too much shade.

Black walnuts provide no source of nitrogen for the grass, but from all indications they are less likely to introduce other limitations to growth. Thus, the net effect of the tree is to be traced to the moderating influence of the light shade, the remineralization of the surface soil through the leaf fall, the more constant soil moisture supply, the better physical condition of the soil, the tree root com-

petition with deep-rooted weeds but not with the grass, and the absence of any condition that severely limits grass growth.

In many cases there is no obvious reason for the yield being as low as it is. This suggests that the grass lacks nutrients which could be supplied by fertilizers or through legumes. From this it would follow that a combination of walnuts with locusts might improve poor pastures more than either species alone, especially if phosphates were supplied. The locusts would supply the nitrogen without being spaced so closely as to introduce the limitations associated with them, and the walnuts would create other favorable conditions.

For every region there should be a theoretical "ideal pasture tree" that would provide a maximum net benefit to the pastures. The studies in southeastern Ohio indicate that such a tree for this region should possess approximately the following characteristics:

Its period of leaf activity should extend only from about June 15 to September 15.

Its canopy should admit approximately 50 per cent of the bright open sunlight to the grass during its period of leaf activity.

Its leaves should be small, fragile, and very high in minerals and nitrogen.

Its root system should extend to a great depth and be highly developed but should feed mainly below the surface 4 inches of soil.

It should be a nitrogen-fixer.

It should be capable of establishment on poor upland sites.

It should possess high commercial value.

With these seven requirements as a standard it is relatively easy to indicate the ways in which trees fall short in their characteristics. The black walnut approaches the ideal in more ways than any other common species. Its greatest weakness is its inability to fix atmospheric nitrogen. The black locust approaches the ideal in more ways than most other common trees, foremost among its desirable characteristics being its ability to fix atmospheric nitrogen.

SUMMARY

Information is presented which indicates that many of the prevailing pastures of southeastern Ohio are improved by the presence of widely spaced black locusts and black walnuts.

The investigation provides evidence that the effect of trees upon pastures is a complex phenomenon that cannot be explained on the basis of any single factor. An evaluation of the more important factors is attempted.

On the basis of the evaluated factors, it seems possible to make reasonably accurate predictions as to the net effect that will follow the introduction of trees into a pasture. The effect will be beneficial or detrimental depending upon the condition of the pasture and the type of tree introduced.

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THE IMPORTANCE OF SODIUM FOR PLANT NUTRITION: III. THE EQUILIBRIUM OF CATIONS IN THE BEET

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In the two preceding articles of this series, attention was drawn to the agricultural importance of sodium, especially for beet culture, and to the distinct difference in effect of certain nitrate fertilizers due to the secondary ions contained therein.[2]

The purpose of the present paper is to examine more closely the question put forward, in the first of these articles, relating to the function of sodium in the beet. This question may be divided into three parts, as follows:

1. Is sodium important merely as a replacement for potassium in the plant?
2. If an adequate quantity of potassium is present, has sodium an independent function in the plant?
3. Must the importance of sodium be regarded from a broader point of view, namely, in relation to the equilibrium of the cations in the plant?

To solve these questions, we grew fodder beets in an artificial adsorptive complex, in which the proportion of the cations could be regulated arbitrarily. The principle and the technique of such experiments with "artificial" soil were worked out by Hudig and Schuffelen between 1937 and 1940 with the object of investigating the effect of the equilibrium of the cations on the plant, but only a provisional account of this research has so far been published.[3]

MATERIAL AND METHODS

Following the method of Hudig and Schuffelen, a carbon preparation ("dusarit") with a highly adsorptive capacity for cations (about 2 m.e. per gm.) was used as an artificial adsorption-complex. By percolating H-dusarit with acetates, Ca-dusarit, Mg-dusarit, K-dusarit, and Na-dusarit can be prepared. At a suspension pH of 6.5, these still contain about 10 per cent H, on the basis of total millequivalents absorbed. By mixing these individual dusarits in varying proportions, adsorptive complexes with suitable ratios of cations can be made. The adsorptive complex is next mixed with silica sand. Because of the great adsorptive capacity of dusarit, a small quantity (4 per cent) is sufficient to provide an "artificial soil" corresponding to a clay soil containing 16 per cent active matter (particles $<2\mu$), but one which has more the character of a humic sandy soil.

[1] The author wishes to thank J. Hudig, director of the institute, for his inspiration and for his continued interest in the carrying out of these investigations. He is also indebted to J. Ch. v. Wesemael for making the analyses for this research.

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Special pots, described in the preceding paper of this series, were employed. They contained a mixture of 14.5 kgm. silica sand with 500 gm. dusarit in addition to 3 kgm. of silica sand for regulating the water supply. The basic fertilizer added comprised 4 gm. $CaHPO_4 \cdot 2H_2O$, 50 mgm. $CuSO_4 \cdot 5H_2O$, 200 mgm. $MnSO_4 \cdot 4H_2O$, and 100 mgm. $FeCl_3$. During the experiment moisture was maintained at 60 per cent of the water-holding capacity.

The basis for comparison of the experiments was a complex of *standard composition* with 8 per cent K, 8 per cent Na, 6 per cent Mg, and 78 per cent Ca (10 per cent H implied), calculated for a normal requirement of the beet plant of about 70 gm. root and about 50 gm. foliage on a dry basis. The composition is expressed in percentage of the total number of milliequivalents of the adsorbed cations (except H). The complex contained 6 per cent Mg and varying proportions of K, Na, and Ca as shown in the following scheme:

With $NaNO_3$ as the nitrogenous fertilizer

1. No Na	4 per cent K	90 per cent Ca
2. No Na	8 per cent K	86 per cent Ca
3. No Na	12 per cent K	82 per cent Ca
4. 8 per cent Na	4 per cent K	82 per cent Ca
5. 8 per cent Na	8 per cent K	78 per cent Ca
6. 8 per cent Na	12 per cent K	74 per cent Ca
7. 16 per cent Na	4 per cent K	74 per cent Ca
8. 16 per cent Na	8 per cent K	70 per cent Ca
9. 16 per cent Na	12 per cent K	66 per cent Ca

With $Ca(NO_3)_2$ as the nitrogenous fertilizer

10. No Na	4 per cent K	90 per cent Ca
11. No Na	8 per cent K	86 per cent Ca
12. No Na	12 per cent K	82 per cent Ca
13. 4 per cent Na	4 per cent K	86 per cent Ca
14. 4 per cent Na	8 per cent K	82 per cent Ca
15. 4 per cent Na	12 per cent K	78 per cent Ca
16. 8 per cent Na	4 per cent K	82 per cent Ca
17. 8 per cent Na	8 per cent K	78 per cent Ca
18. 8 per cent Na	12 per cent K	74 per cent Ca
19. 16 per cent Na	4 per cent K	74 per cent Ca
20. 16 per cent Na	8 per cent K	70 per cent Ca
21. 16 per cent Na	12 per cent K	66 per cent Ca
22. 24 per cent Na	4 per cent K	66 per cent Ca
23. 24 per cent Na	8 per cent K	62 per cent Ca
24. 24 per cent Na	12 per cent K	58 per cent Ca

The nitrogenous fertilizer was applied to each pot[4] at the rate of 5 gm. N, half at the beginning of the experiment and half as a top-dressing on August 5. All experiments were run in triplicate with the Barres variety of fodder beet, planted in the pots June 4 and harvested October 14, 1940.

[4] As in the experiments described in the preceding paper of this series, all treatments included equivalent quantities of boron.

RESULTS

Growth development

Especially after the N top-dressing, distinct differences in rate and habit of growth became apparent between the $NaNO_3$ and the $Ca(NO_3)_2$ plants. These differences were identical with those described in the second paper of this series. The most interesting feature in this respect was the development of the plants of the $Ca(NO_3)_2$ series. As the Na content of the complex increased, the "calcium type," characterized chiefly by compressed habit and dark green color of foliage, faded in the "sodium type," with its drooping foliage of a light green color. In some instances the reaction to the equilibrium of the ions was so specific that the outer leaves rather resembled the Na type and the inner ones the Ca type, corresponding with the situation before and after the top-dressing. Increase in the K level influenced the foliage only in the pots containing no Na, but it had a marked favorable effect on the production of beet.

Yields

The yields for each pot are shown in table 1. In experiments such as this, with only one plant per pot, the yield data for replicates differ widely, although as will be seen in subsequent analyses, definite conclusions can be drawn concerning the mutual relationships between the ions.

The trend of the yields is most strikingly shown in the fresh weights of the beets. Here the sodium fertilizer, as well as the high content of Na in the complex, produces a high yield level. Calcium nitrate has a detrimental effect on the beet yield, but this can be neutralized gradually by increase of the Na content in the complex, and potassium is still more active in this respect.

The trend of the dry-matter yields of the beets is slightly less evident, because in the $Ca(NO_3)_2$ series, the 12 per cent K treatment produced much higher yields than those in the $NaNO_3$ series. Otherwise, the trend is roughly the same as that of the fresh yields and only a displacement of the yields with $Ca(NO_3)_2$ took place. This is accounted for the by the fact that the dry-matter content of the beets of the $Ca(NO_3)_2$ series is higher than that of the beets of the $NaNO_3$ series. The content of sugar fluctuates with the content of dry matter. Calcium promotes, therefore, a higher content of dry matter and of sugar than does sodium. Because of the higher beet weight in the $NaNO_3$ series, however, the total yield of sugar invariably counterbalances that of the beets in the $Ca(NO_3)_2$ series.

Table 1 shows also the dependence of the dry weight of foliage upon the composition of the complex and upon fertilizer treatment. It is clear that sodium tends to increase the yield of foliage, which averages 55.3 gm. for all $NaNO_3$ plants, in comparison with the 45.6 gm. for no Na, 51.3 gm. for 4 per cent Na, 48.2 gm. for 8 per cent Na, 54.2 gm. for 16 per cent Na, and 53.7 gm. for 24 per cent Na in the $Ca(NO_3)_2$ series.

That potassium does not show a similar tendency is evident from the following averages:

	4 per cent K	*8 per cent K*	*12 per cent*
$NaNO_3$ series .... *gm.*	56.3	53.4	56.1
$Ca(NO_3)_2$ series .... *gm.*	50.8	49.6	51.4

TABLE 1

Yield of fodder beets, dusarit pot experiment, 1940

POT NUMBER*	BEET			FOLIAGE			SUGAR	TOTAL, DRY WEIGHT
	Fresh weight	Dry weight	Dry matter content	Fresh weight	Dry weight	Dry matter content		
	gm.	*gm.*	*per cent*	*gm.*	*gm.*	*per cent*	*gm.*	*gm.*
1 A	878	112.6	12.8	489	70.7	14.45	78.1	183.3
1 B	731	91.8	12.55	475	66.1	13.9	51.2	157.9
1 C	755	69.2	9.2	220	45.6	20.7	25.7	114.8
2 A	564	83.6	14.8	472	66.6	14.1	49.6	150.2
2 B	778	97.2	12.5	420	58.0	13.8	62.2	155.2
2 C	978	137.2	14.0	415	50.3	12.1	92.9	187.5
3 A	860	114.0	13.3	679	78.3	11.5	73.1	192.3
3 B	905	118.5	13.1	285	46.8	16.4	74.2	165.3
3 C	1,020	135.4	13.3	542	66.9	12.3	67.3	202.3
4 A	850	110.9	13.0	535	55.4	10.35	57.8	166.3
4 B	1,084	130.3	12.0	480	57.8	12.0	95.4	188.1
4 C	930	129.8	13.95	422	47.8	11.3	80.0	177.6
5 A	812	117.9	14.5	341	58.3	17.1	79.6	176.2
5 B	905	98.9	10.9	140	35.1	25.0	39.8	134.0
5 C	1,071	147.8	13.8	450	50.1	11.15	83.5	197.9
6 A	993	153.1	15.4	612	60.6	9.9	91.4	213.7
6 B	923	113.5	12.3	432	52.3	12.1	64.6	165.8
6 C	862	99.3	11.5	447	43 5	9.7	47.4	142.8
7 A	851	94.9	11.2	506	55.2	10.9	60.4	150.1
7 B	.	...	...	..	...	....	...	...
7 C	802	87.7	10.9	282	53.5	19.0	52.1	141.2
8 A	952	130.2	13.7	440	51.4	11.7	78.1	181.6
8 B	625	72.4	11.6	355	55.3	15.55	31.9	127.7
8 C	1,125	155.6	13.8	374	55.4	14.8	94.5	211.0
9 A	782	92.4	11.8	322	39.1	12.1	46.9	131.5
9 B	1,069	141.6	13.25	406	63.8	15.7	88.7	205.4
9 C	880	101.3	11.5	442	53.1	12.0	69.5	154.4
10 A	524	73.1	13.95	171	41.9	24.5	44.0	115.0
10 B	524	82.1	15.65	262	38.1	14.5	47.5	120.2
10 C	521	67.7	13.0	100	37.9	37.9	32.8	105.6
11 A	640	106.9	16.7	390	41.0	10.5	61.1	147.9
11 B	698	107.1	15.3	340	47.3	13.9	64.2	154.4
11 C	698	104.8	15.0	353	56.6	16.0	64.2	161.4
12 A	717	104.2	14.55	390	50.1	12.85	57.4	154.3
12 B	785	81.4	10.4	456	53.0	11.6	51.0	134.4
12 C	926	110.2	11.9	408	44.9	11.0	69.5	155.1
13 A	471	70.3	14.9	398	47.8	12.0	42.9	118.1
13 B	642	89.1	13.9	384	44.3	11.5	50.7	133.4
13 C	536	88.3	16.45	510	57.8	11.3	50.6	146.1
14 A	563	88.3	15.7	425	46.9	11.0	49.5	135.2
14 B	618	134.2	21.7	555	76.1	13.7	85.9	210.3
14 C	438	73.2	16.7	292	39.3	13.4	32.4	112.5
15 A	750	118.6	15.8	461	51.6	11.2	69.0	170.2
15 B	763	102.9	13.5	320	40.8	12.75	63.3	143.7
15 C	721	116.3	16.1	421	56.8	13.5	59.3	173.1

* A, B, and C are replicates.

TABLE 1—*Concluded*

POT NUMBER*	BEET			FOLIAGE			SUGAR	TOTAL, DRY WEIGHT
	Fresh weight	Dry weight	Dry matter content	Fresh weight	Dry weight	Dry matter content		
	gm.	*gm.*	*per cent*	*gm.*	*gm.*	*per cent*	*gm.*	*gm.*
16 A	461	85.2	18.5	281	57.7	20.5	42.4	142.9
16 B	523	78.9	15.1	397	51.5	13.0	41.8	130.4
16 C	582	80.8	13.9	332	42.0	12.65	43.1	122.8
17 A	904	118.2	13.1	320	45.2	14.1	70.5	163.4
17 B	746	124.9	16.7	84	32.0	38.1	58.9	156.9
17 C	671	127.3	19.0	545	56.2	10.3	72.5	183.5
18 A	1,132	157.0	13.9	471	42.6	9.05	88.3	199.6
18 B	702	123.4	17.6	543	67.3	12.4	69 5	190.7
18 C	926	146.9	15.85	350	39.0	11.1	85.2	185.9
19 A	693	110.9	16.0	415	51.6	12.4	65.8	162.5
19 B	556	89.1	16.0	378	48.9	12.9	49.5	138.0
19 C	731	119.5	16.3	482	64 0	13.3	66.5	183.5
20 A	460	56.5	12 3	495	55.9	11.3	28.5	112.4
20 B	789	99.2	12.6	416	50.7	12.2	57.6	149.9
20 C	840	120.9	14.4	531	55.5	10.4	68.0	176.4
21 A	771	129.4	16.8	441	61.4	13.9	74.0	190.8
21 B	854	146.5	17.15	420	53.3	12.7	77.7	199.8
21 C	915	148.2	16.2	382	46.6	12 2	83.3	194.8
22 A	675	70.4	10.4	332	46.8	14.1	35.8	117.2
22 B	1,119	169.9	15.2	631	62.7	9 95	113.0	232.6
22 C	737	115.8	15 7	518	68.6	13.25	67.1	184.4
23 A	960	114.1	11.9	332	42.1	12.7	58.6	156.2
23 B	840	119.1	14.2	400	48.2	12.1	70.6	167.3
23 C	892	140.4	15.7	470	51.2	10.9	76.7	191.6
24 A	598	85.4	14.3	400	54.4	13 6	51.4	139.8
24 B	681	82.3	12.1	361	52.4	14 5	35.4	134.7
24 C	782	129.0	16 5	405	56.8	14.0	73.5	185.8

Analyses

The composition of foliage and beets is shown in table 2. To demonstrate that this composition encompasses a complete scale of proportions, the values have been classified in the most logical order, viz., according to ascending Na content, separately for all series with 4 per cent K, 8 per cent K, and 12 per cent K, respectively. There are distinct correlations between the level of a given ion in the complex and its assimilation by the plant, but in addition, this assimilation appears to be strongly dependent on the level of the other ions. The Ca ion represents the most striking example in this connection. When the Ca content of the complex and that of the fertilizer are added, the total in the pots of the $Ca(NO_3)_2$ series ranges from 1260 (900 plus 360) to 940 (580 plus 360) m.e. Between these extreme values, we find the following Ca contents of foliage and beet, in milliequivalents per 100 gm. dry matter:

POT	Ca PER POT, M.E.	Ca CONTENT OF FOLIAGE	Ca CONTENT OF BEET
10	1,260	315	29
22	1,020	86	16
11	1,220	273	31
23	980	83	12
12	1,180	184	42
24	940	63	12

These figures show that the univalent ions K and Na exert a strong influence on the activity of Ca. This may be explained simply in the present instance as

TABLE 2

K, Na, and Ca content of foliage and beet roots produced in dusarit pot experiment

Averages per series of 3 pots, in m.e. per 100 gm. dry matter

POT NUMBER	K CONTENT OF COMPLEX	FOLIAGE			BEET		
		K	Na	Ca	K	Na	Ca
	per cent						
10	4	73	31	315	33	5	29
13		31	88	238	27	13	35
16		36	135	160	23	28	43
19		36	237	130	15	38	21
22		29	294	86	15	64	16
1		37	307	67	16	87	13
4		31	387	56	16	74	9
7		32	390	38	16	93	7
11	8	71	33	273	32	2	31
14		85	103	177	32	6	32
17		55	170	161	38	18	17
20		90	236	105	39	49	22
23		52	340	83	29	52	12
2		47	299	71	33	48	10
5		47	254	57	32	66	7
8		41	409	42	30	72	7
12	12	115	39	184	51	3	42
15		111	106	157	47	9	19
18		95	161	154	39	15	20
21		96	262	98	35	24	11
24		86	310	63	41	43	12
3		53	304	51	37	48	8
6		63	301	47	40	60	8
9		60	413	39	40	69	6

follows: The complex poor in Ca (580 m.e. Mg, 120 m.e. K, and 240 m.e. Na) can absorb by exchange all the Ca from the fertilizer (360 m.e.), as a result of which the activity of Ca declines considerably. In contrast, the complex rich in Ca (900 m.e. Ca, 60 m.e. Mg, and 40 m.e. K) can absorb a maximum of 100

m.e. of the Ca added by the fertilizer, and consequently, a large part of this remains in solution. This Ca represents a high Ca activity and causes, therefore, a strong assimilation by the plant.

This explanation has, of course, only a limited validity and does not apply to the other ions. It makes clear, however, for the example chosen, the connection between the composition of the complex, and of the fertilizer, and the assimilation of ions by the plant. In a recent article, Loosjes and Schuffelen[5] suggested a method for measuring the activities of ions of suspensions. As this

TABLE 3

Cation content of beets grown on soil fertilized with different forms of nitrate supplemented by different quantities of potassium

Averages per series of four pots in experiment 3 (part II of this series), in m.e. per 100 gm. dry matter

POT NUMBER*	FOLIAGE			BEET		
	K	Na	Ca	K	Na	Ca
1	20	413	67	25	97	18
2	30	385	61	28	71	19
3	42	397	67	39	112	14
4	67	376	63	37	88	14
5	65	400	69	57	104	15
6	28	99	199	33	20	44
7	55	101	210	45	14	72
8	99	106	191	60	16	55
9	105	98	203	67	18	44
10	156	100	183	65	14	43
11	32	98	190	33	17	60
12	50	97	191	42	15	51
13	76	94	216	49	15	36
14	104	93	172	48	11	38
15	127	86	166	65	14	53

* Pots 1-5 were fertilized with $NaNO_3$; pots 6-10, with $Ca(NO_3)_2$; pots 7-15, with $NH_4NO_3 + CaCO_3$. Pots 1, 6, and 11 received no K applications; pots 2, 7, and 12, 918 mgm. K; pots 3, 8, and 13, 1836 mgm. K; pots 4, 9, and 14, 2754 mgm. K; and pots 5, 10, and 15, 3672 mgm. K.

measurement provides the means of determining a more general relation between composition and assimilation of ions, it may be of great importance for both agricultural chemistry and plant physiology.

Comparison of the assimilation figures of foliage and beet reveals a striking difference in cation content. Moreover, *the foliage contains proportionately more sodium and calcium, and the beet more potassium,* as may be gathered from the proportions of Na:K and Ca:K shown in the following figures:

[5] Loosjes, R., and Schuffelen, A. C. 1941 *Proc. K. Akad. Amsterdam* 44: 475.

		Na : K	Ca : K
$Ca(NO_3)_2$	Beet	0.1– 4.4	0.3–1.8
	Foliage	0.3–10.0	0.7–7.8
$NaNO_3$	Beet	1.3– 6.0	0.2–0.8
	Foliage	4.8–12.4	0.6–1.8

In itself, this is an indication of the degree of importance of the three cations to beets and foliage.

Equilibrium of ions and production

A clearer idea of the correlations existing between yield and equilibrium of ions may be obtained by plotting these figures in a triangular graph.[6] Figures

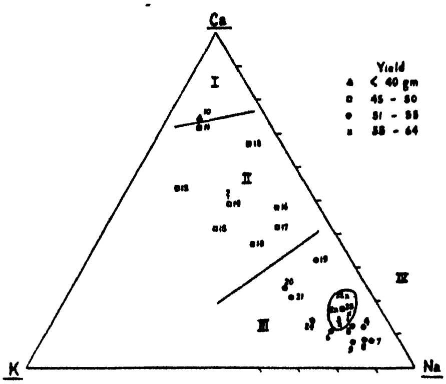

FIG. 1. THE K-, Ca-, AND Na-ION CONTENT OF THE FOLIAGE OF FODDER BEETS IN RELATION TO YIELD

Ion contents shown as percentages of the total number of milliequivalents of the three cations absorbed per 100 gm. dry matter. The points of the triangle labeled K, Ca, and Na represent 100 per cent of the respective cations; the points opposite, 0 per cent. The yield areas are as follows: I, low (<40 gm.); II, moderate (45–50 gm.); III, good (51–55 gm.); IV, high (58–64 gm.)

1, 2, and 3 show successively the composition of foliage, of beet, and of the whole plant, in percentages of the number of milliequivalents absorbed, each plotted point being indexed according to its yield class. The graphs thus show at a glance the connection between yield and relationship of ions.

Foliage. The Ca–K–Na diagram of foliage composition (fig. 1) subdivides logically into four areas, viz.:

I. An area of high Ca content, in which falls only pot 10 with a *low* yield (<40 gm.).
II. A large area of intermediate Ca and Na content, to which belong all *moderate* yields of foliage (45–50 gm. inclusive; pot 14 is doubtful, because 14B fell out).
III. An area of high Na content, comprising the *good* foliage yields (51–55 gm. inclusive).

[6] For simplicity, it is assumed that in a complex having a constant level of Mg and H, the effect of these ions may be disregarded.

IV. A small area included in area III and comprising the *high* foliage yields (58–64 gm. inclusive; pot 23 constitutes an exception). This small area of maximum yields might be imagined in space as a highland slanting gradually to the Ca and Na sides.

The equilibrium most favorable for the foliage lies, therefore, in area IV, i.e., with approximately 10 per cent K, 20 per cent Ca, and 70 per cent Na. More Ca is unfavorable for this equilibrium, and more Na causes the yield to decline slightly. Furthermore, potassium, provided it is not *too* low, seems not to play a dominant role in the foliage. The Na:Ca relation is, therefore, the primary factor in the development of foliage.

Beet. For beets, different yield areas (fig. 2), similar to those for foliage, can also be distinguished. Four of these areas correspond in some degree with

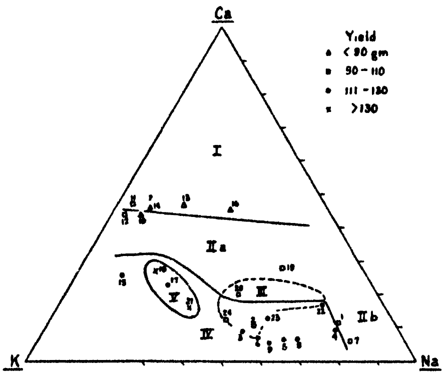

FIG. 2. THE K-, Ca-, AND Na-ION CONTENT OF THE BEET ROOT IN RELATION TO YIELD

Ion content shown as percentages of the total number of milliequivalents of the three cations absorbed per 100 gm. dry matter. The points of the triangle labeled K, Ca, and Na represent 100 per cent of the respective cations: the points opposite, 0 per cent. The yield areas are as follows: I, low (<90 gm.); II, moderate (90–110 gm.); III, transition, with a wide spread; IV, good (111–130 gm.); V, high (>130 gm.)

those of the foliage, and in addition we find a fifth area, probably having a separate significance.

I. This area again comprises the *low* yields (<90 gm.). In it we find a larger number of pots (Nos. 10, 13, 16, and 14?), and the area itself is more extensive than area I in figure 1. This situation implies that a high Ca content is more injurious for the beet than for the foliage.

II. This area represents the *moderate* yields (90–110 gm.) and constitutes a narrow strip bordered on the upper side by the high Ca content values and passing on the right into an area of very high Na content (IIb). *The shape of this area is explained by the fact that, on the one hand, a high Ca content has a depressing effect on the yield* (irrespective of whether this is expressed as fresh or dry weight), *and on the other hand, a high Na content increases the fresh yield but induces a low percentage of dry matter, and consequently the yield of dry matter is moderate.*

III. This area represents a transition from the area of moderate yields to the areas of higher yields. To area III belong pots 2, 20, and 24, which produced, on an average, a *moderate* yield, and pots 6 and 22 with a *good* average yield. As already

mentioned, in a crop such as beets and with but few replicates, a high average error must be expected. For this reason one must be cautious in averaging the data. In a mutual relationship such as that depicted here, most points check one another, and the location of the areas is, on the whole, open to question. In none of the other areas, however, have the results such a wide spread as in III (the mean error of the average in all these instances is >15 per cent; that for all other areas, <15 per cent). It seems plausible, therefore, that this is a characteristic feature of the transition area. We are apparently dealing with a somewhat *unstable situation* which may take either a favorable or an unfavorable turn. In the meantime, one should be cautious in drawing conclusions. The available data are not sufficiently extensive to indicate exactly the dividing lines between low, moderate, good, and high. For this reason, area III has been allowed to overlap areas II and IV; this suffices for a first approximation.

IV. This area shows the *good* yields (111–130 gm.). On the K side, but few pots are found.

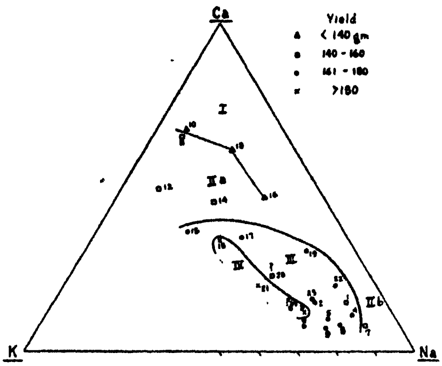

Fig. 3. The K-, Ca-, and Na-Ion Content of the Whole Fodder Beet Plant in Relation to Yield

Ion content shown as percentages of the total number of milliequivalents of the three cations absorbed per 100 gm. dry matter. The points of the triangle labeled K, Ca, and Na represent 100 per cent of the respective cations; the points opposite, 0 per cent. The yield areas are as follows: I, low (<140 gm.); II, moderate (140–160 gm.); III, good (161–180 gm.); IV, high (>180 gm.)

V. Again, as in figure 1, a small area of *high* yields (>130 gm.), in this instance area V, is encompassed in the area of good yields. The beet requires but small quantities of calcium. Both the position of area V and the shape of area IV indicate that potassium is the most important element here, although good yields are also obtainable with a high ratio of Na:K. If this ratio becomes *too* high, however, a less favorable situation arises, because of the disproportionately large production of foliage and the disproportionately low dry matter content of the beets. *The most favorable equilibrium of ions for the beet lies in area V with about 50 per cent K, 25 per cent Ca, and 25 per cent Na.*

Total yield of dry matter. Figure 3, depicting the dry matter yield of the whole plant, has four main areas, as follows:

I. Area of *low* yields (<140 gm.)
II. Area of *moderate* yields (140–160 gm.)
III. Area of *good* yields (161–180 gm.)
IV. Area of *high* yields (>180 gm.)

As was to be expected, these areas occupy a position intermediate to those of foliage and of the beet. *The most favorable equilibrium of ions for the total beet plant, and likewise the area of good yields, has moved entirely to the sodium side.*

Sugar yield. Sugar yields may be grouped similarly to yields of dry matter, since the former is directly related to the latter. If yield limits are taken as x = > 70 gm., ● = 61 − 70 gm., □ = 50 − 60 gm., and △ = < 50 gm., figure 3 shows only the following changes: point 4 becomes x, 11 becomes ●, and 22 becomes x. In general this graph also reflects, therefore, the sugar yield.

THE SODIUM FUNCTION

Strictly speaking, the results imply the answers to the questions raised at the beginning of this paper. They may be more definitely stated as follows:

1. In the beet root, sodium is important not only in the replacement of potassium, but also as a stimulant to production; good production is impossible without Na. For instance, pots 10, 11, and 12 produced moderate yields only, in spite of the high K content of both foliage and beet.

2. In the foliage, sodium has an almost independent function. The fact that good development is impossible without Na is still more pronounced in the foliage than in the beet root. It is probable that sodium does *not* play the part here of a replacement.

3. Such concepts as "replacement" and "independent function" assume a different degree of importance in the equilibrium of cations. Here each element plays its own part, sometimes in relatively larger, sometimes in relatively smaller, quantities. The inclination has been too great to evaluate the importance of an element according to its absolute quantity. In the equilibrium of cations, however, the decisive factor is the exact proportions rather than the absolute quantities. It now appears that the proportions of sodium may not be disregarded any more than the proportions of other cations. Moreover, the beet provides an example also of the extreme importance of absolute quantities of sodium.

So far we have dealt only with the relationship between yields and equilibrium of ions in the plant. In agricultural practice it is of primary importance to know how the yields depend on the composition of the complex and on the fertilizer applications. It is not within the scope of this paper to depict this relationship graphically, because in a Ca–K–Na diagram all points representing the composition of the complex occur in a narrow strip along the Ca–Na side.[7] The principle, advanced by Loosjes and Schuffelen, that the assimilation of ions be considered as dependent on the ion activities of the complex, might lead to results, if an attempt were made to weigh the yields directly against the ion activities.

For the present, figure 3 provides the best picture, as it implies almost all correlations. Unfortunately, little statistical material is available on the relative richness of K in Dutch soils. The following rough comparison might

[7] Schuffelen could do this for experiments with oats, because the components of the complex were more varied; the fertilizer applications, however, cannot be indicated.

be made between the K level of Dutch soils and the dusarit mixtures used in these experiments:

K LEVEL	DUSARIT MIXTURE	DUTCH SOILS	FREQUENCY
	m.e. K per 100 gm. active fraction		
I. Low	2	0–2/3	Normal
II. Normal	4	3–5	Rarer
III. High	6	>5	Extremely rare

Large areas of the Dutch sandy and river-clay soils are to be classified under I. Moreover, the river-clay soils, such as those along the Rhine and Meuse Rivers, are distinguished by their capacity to fix K. Young sea-clay soils may contain

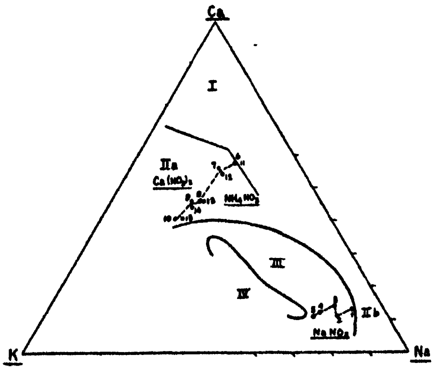

FIG. 4. CATION CONTENTS AND YIELDS OF BEETS ON HUMUS SANDY SOIL

These data, from experiment 3 (part II of this series), fit into the scheme of figure 3. The values of $NaNO_3$ all lie in the good area (III); those of $(CaNO_3)_2$ and NH_4NO_3 + $CaCO_3$, in the moderate area (II). Although the K application was very high, it was not quite adequate for an area of better yields

appreciable quantities of K, but many of the older sea-clay soils are low in K. A large part of the Dutch soils belong, therefore, to class I.

An example, showing some conformity with practice, is to be found in the analyses of pot experiment 3, dealt with in the second paper of this series. When these figures are worked into a diagram in which the limits for the total yield (according to figure 3) are indicated, virtually all the points for applications of $Ca(NO_3)_2$ and of NH_4NO_3 + $CaCO_3$ fall within area IIa, and those for $NaNO_3$ fall entirely within area III. The composition of the complex of this soil (a humus sandy soil with a pH value of 6.5, 3.4 per cent humus, and 4.3 per cent clay) was as follows, per 100-gm. fraction:

54.0 m.e. Ca,	i.e., 82.8 per cent of the total
3.0 m.e. K,	i.e., 4.6 per cent of the total
3.0 m.e. Na,	i.e., 4.6 per cent of the total
0.9 m.e. NH_4,	i.e., 1.4 per cent of the total
4.3 m.e. Mg,	i.e., 6.6 per cent of the total

Although, as regards K and Na level, this soil cannot be classified as poor, it responds strongly to the nitrate application, as is clear from the position of the points in figure 4. The equilibrium of cations is quite different for the three nitrate fertilizers applied, and this causes the yields to differ appreciably (cf. table 2, paper II of this series). For the yields with $Ca(NO_3)_2$ or with NH_4NO_3 to fall into the favorable area, the K additions must be very high, and even then the points may occur too far to the left in the diagram. When $NaNO_3$ is applied, the only precaution necessary is to add enough K to avoid the unfavorable area IIb, and, therefore, one can be most economical with the K application.[8] It is not yet possible to judge how far mixture of fertilizers might be carried to produce still more favorable results.

In general, it may certainly be said that in agricultural practice it is very difficult to obtain the high K level required for area IV, except on soils naturally rich in K.

SUMMARY

To study the equilibrium of cations, fodder beets were grown on an "artificial soil," of which the composition of the adsorption complex could be regulated arbitrarily. The principle of these experiments was based on the work of Hudig and Schuffelen.

The equilibrium of ions in the beet, dominated largely by the ions K, Na, and Ca, was correlated graphically with the production. The results indicate that foliage and root react differently to the proportion of ions in the soil.

In the equilibrium of ions in the foliage, sodium plays a very important part; in the equilibrium of ions in the root, potassium is very important. Sodium can replace potassium to a large extent, however, in the beet root without detriment to good production and is, under all circumstances, an important factor in the equilibrium of ions. Calcium, on the contrary, when present in relatively large quantities, very soon has a detrimental effect on the production of both foliage and root. For practical beet culture sodium should, therefore, be preferred as the secondary ion in fertilizers; it has a K-conserving effect.

[8] For present, we cannot go into the importance to animal nutrition of the equilibrium of ions in beets used for fodder. In the long run, this will certainly become an important factor in evaluating the product.

LABORATORY STUDY OF THE RESPONSE OF 2- AND 4-ELECTRODE PLASTER OF PARIS BLOCKS AS SOIL-MOISTURE CONTENT INDICATORS

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Information being amassed on the optimum irrigation practice for most of the crops grown in the Western States is based on quantitative data on soil moisture at different depths during the growing season. The standard procedure of determining these data includes the preliminary steps of removing the soil samples to the laboratory, weighing, drying, and reweighing. Generally the labor involved is prohibitive for large-scale commercial practice.

A direct reading method that will enable the grower to determine the soil-moisture content in the field as easily and quickly as if he were merely reading a meter is needed. A number of methods have been proposed. Of these, several, such as the following, seem to show promise.

One of the earliest (2, 4, 7) was to determine the electrical resistance of the soil by placing in it only two electrodes and using an alternating current to avoid polarization. The general conclusion by soil workers was that the contact resistance between the electrodes and the soil may be too erratic (for an expansion or contraction of the soil immediately adjacent to the electrodes will lower or raise the contact resistance) and the variations in salt content of the soil solution may be too great to permit the use of this method for measuring variations in soil-moisture content. The original workers, however, do not seem to have thought so.

Later we find the proposal and investigation of the four- or multiple-electrode method (3, 6), so arranged as to eliminate the erratic contact resistance between the electrodes and the soil but still leaving unanswered the possible influence of variations in salt concentration.

Finally, we again find the use of the 2-electrode method (1), but now both the electrodes instead of being imbedded directly in the soil are imbedded close together in a plaster of paris block which itself is placed directly in the soil. The value of the electrical resistance across the electrodes is taken as a measure of the moisture content of the soil. A number of advantages of this method aside from cheapness and simplicity have been pointed out (1). It considerably reduces a number of the difficulties arising from variations of composition, texture, and salt concentration in the soil. Also, it should not require a separate calibration for each soil, since it probably measures the tightness with which the water is held. That is, at the permanent wilting percentage of all soils the plaster of paris blocks should all have the same electrical resistance. Likewise, at the moisture equivalent of all soils the blocks should all have the same electrical resistance, but this should be lower than that at the permanent wilting percentage.

Literature on this method of indicating soil-moisture content still leaves un-

answered some of the most important questions concerning the characteristics of the blocks.

The first question is: How reproducible are the measurements made by this method? For example, suppose we find at a moisture content near the permanent wilting percentage of the soil that the resistance is 40,000 ohms. Then suppose, after irrigating the soil one or more times, we again make a determination of the soil-moisture content and the resistance and find the latter to be 40,000 ohms, how close will the value of the soil-moisture content in the latter case be to the former? If the difference is too great, obviously the method is useless as a soil-moisture content indicator.

Suppose we find that the method gives reproducible results under certain conditions, another question is: How long does it take the block to establish a moisture-content equilibrium with the soil surrounding it? It is well known that, particularly at the lower moisture contents, moisture moves increasingly more slowly as the moisture content is decreased. If it moves too slowly, a plant may die long before the instrument indicates that the soil has reached the permanent wilting percentage.

Also, how much of the change in the resistance of the block, caused by a change of moisture content, is due to the change in contact resistance between the electrodes and the plaster of paris, and how much is due to the change in the conductivity of the plaster of paris itself? And finally, how much is the electrical resistance of the block changed by a change in the separation of the electrodes?

The purpose of the present investigations is to answer the foregoing questions. In order to do this, we have prepared a number of what we shall term "4-electrode plaster of paris blocks," one of which is schematically shown in figure 1. Its construction is similar to the 2-electrode block already described (1) except that its width is twice as great and that it has four, instead of two, equidistant parallel electrodes all lying in the midplane of the block.

The theory and use of the 4-electrode principle has been given in another application (3, 6) where it was shown that any changes in the contact resistance between the plaster of paris and the electrodes are eliminated entirely and the value of the resistance obtained is determined alone by the surrounding medium. It was shown that if R_1, R_2, R_5, and R_6 represent the electrical resistances in ohms measured across the terminals of electrodes 1–2, 1–3, 2–4, and 3–4 respectively as shown in figure 1, then μ_1, the electrical resistance of the medium surrounding the electrodes is given by

$$\mu_1 = K\,[(R_2 + R_5) - (R_1 + R_6)] \qquad (1)$$

in ohms where, for an infinite and homogeneous medium, K depends only on the distance apart and the shape of the electrodes.

Since we shall apply the equation to a medium which is not infinite and is not homogeneous, but instead has the shape shown in figure 1, K will depend also upon the shape of the plaster of paris blocks. Since all the blocks are made alike, the effect of the shape of the block on the value of K will also be alike for all blocks, and thus the results from all the blocks should be comparable. If μ_1 is

defined as a measure of the electrical resistance of the plaster of paris alone, then (as will be shown in the appropriate place later) K must also in some cases depend partly on the moisture content of the soil adjacent to the block. We shall therefore redefine μ_1 to be a measure of the combination of (a) the electrical resistance of the plaster of paris and (b) the soil mass immediately surrounding the block. The latter will be shown to be negligible in the case of most practical importance. A little consideration will show that this definition is consistent with the theory previously given (3, 6). Both resistances R_1 and R_6 should, of course, behave in the same way, and R_2 and R_5 in approximately the same way, as the 2-electrode blocks of Bouyoucos. In the following investigation, 4-electrode blocks were used throughout, thus enabling us to observe simultaneously the behavior of the 4-electrode block resistance μ_1 and the 2-electrode block resistances given by either R_1 or R_6.

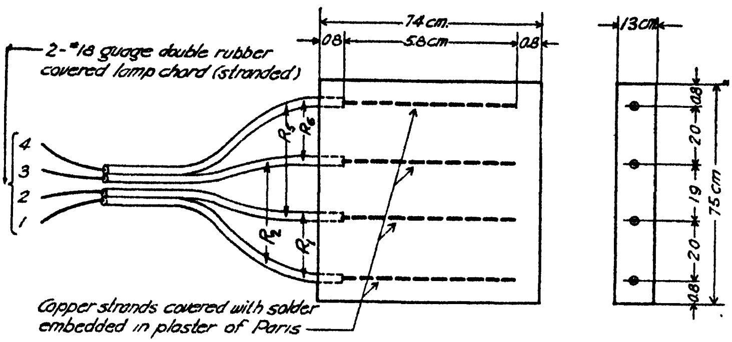

FIG. 1. DIMENSIONS OF THE 4-ELECTRODE PLASTER OF PARIS BLOCK

For brevity, henceforth we shall drop the constant K in equation 1, since K is the same for all blocks, and call the quantity in brackets the 4-electrode resistance of the plaster of paris block. That is

$$\mu_1 = [(R_2 + R_5) - (R_1 + R_6)] \tag{2}$$

PREPARATION OF THE PLASTER OF PARIS BLOCKS

The instrument used in the determination of the electrical resistance of the plaster of paris blocks was the traditional A.C. Wheatstone bridge circuit using the General Radio Type 813 audio-oscillator emitting a frequency of 1000 cycles, the Leeds and Northrup 4-dial resistance boxes, and one stage of amplification, using an R.C.A. No. 32 amplifier tube, to feed into the head phones.

The plaster of paris blocks were prepared from McKesson Robbins plaster of paris for splints, casts, and impressions. Any other of equal quality undoubtedly would do as well. They were cast in carefully made forms, all alike. The electrodes were held firmly in place while the two ends of the block were cast, thus embedding the ends of the electrodes in a matrix. About 15 minutes after the ends of the electrodes were cast in place and before the plaster of paris had set, the forms holding the electrodes in place were removed and the equidistance of

the spacing of the electrodes was again checked. About 5 minutes later all the intervening space was filled. The plaster of paris for each of these pourings was prepared separately. In each case, the amount of water and plaster of paris had been measured out beforehand. Sixty seconds before each pouring, the water and plaster of paris were poured together, stirred for about 45 seconds, and then rapidly poured into the forms. Distilled water was always used. The ratio of the weight of plaster of paris to water always was taken as 1.18 to 1.00. The plaster of paris was stirred very gently in the forms immediately after pouring to ensure that it would fill all corners. An excess was poured into the forms so that all bubbles and scum would rise into it and could be trimmed off after the block had been thoroughly dried in the forms.

To ensure unquestioned similarity in characteristics of the blocks, such factors as the proportion of plaster of paris to water, the mixing time, and the pouring time must be carefully reproduced in the making of each block. Though deviations from the foregoing procedure may produce a block with good characteristics, the method described was the one selected after many trials. The important thing is to adhere to the same procedure in making all the blocks.

LAG IN RESPONSE OF PLASTER OF PARIS BLOCKS

Our experimental results show that, when the blocks are calibrated as described elsewhere (1), there is a tremendous lag in their response to the moisture content of the surrounding soil when this is near the permanent wilting percentage. The calibration method there employed was to place the block, previously saturated in distilled water, on a layer of the soil in a shallow pan, and cover the block completely with more soil. The entire contents of the pan were then saturated with distilled water, after which more soil was heaped on top to form a mound. As drying proceeded, the soil was compacted so that a close contact was assured between the blocks and the soil. After equilibrium was attained, as indicated by a constant resistance across the terminals of the block, the resistance was noted and the moisture content of the thin layer of soil immediately adjacent to the block was determined by its loss in weight upon drying. Other pairs of resistance–moisture-content values on the calibration curve were obtained similarly by allowing the drying to proceed to varying stages.

We followed a somewhat similar calibrating procedure but were unable to obtain an equilibrium value for the electrical resistance of the blocks when we dealt with soils at lower moisture contents in the vicinity of the permanent wilting percentage.

We prepared a series of soil samples, each of about 12 kgm. dry weight but at different moisture contents, and placed them in buckets. In each were embedded several plaster of paris blocks which had previously been saturated with distilled water and from which the excess water on the outside had been wiped off. The top of the soil surface was then sealed with paraffin and almost the entire bucket immersed in a constant temperature bath. The electrical resistance of the blocks was determined daily. The results for the 2-electrode blocks are given in figure 2; for the 4-electrode blocks, in figure 3.

Since, for the soil used, the range of moisture content readily available to plants is 8.4 per cent (the moisture equivalent is 16.8 per cent, the permanent wilting percentage is 8.4 per cent) the curves for the 2-electrode blocks show that even after 1 month the plaster of paris block does not attain equilibrium if sur-

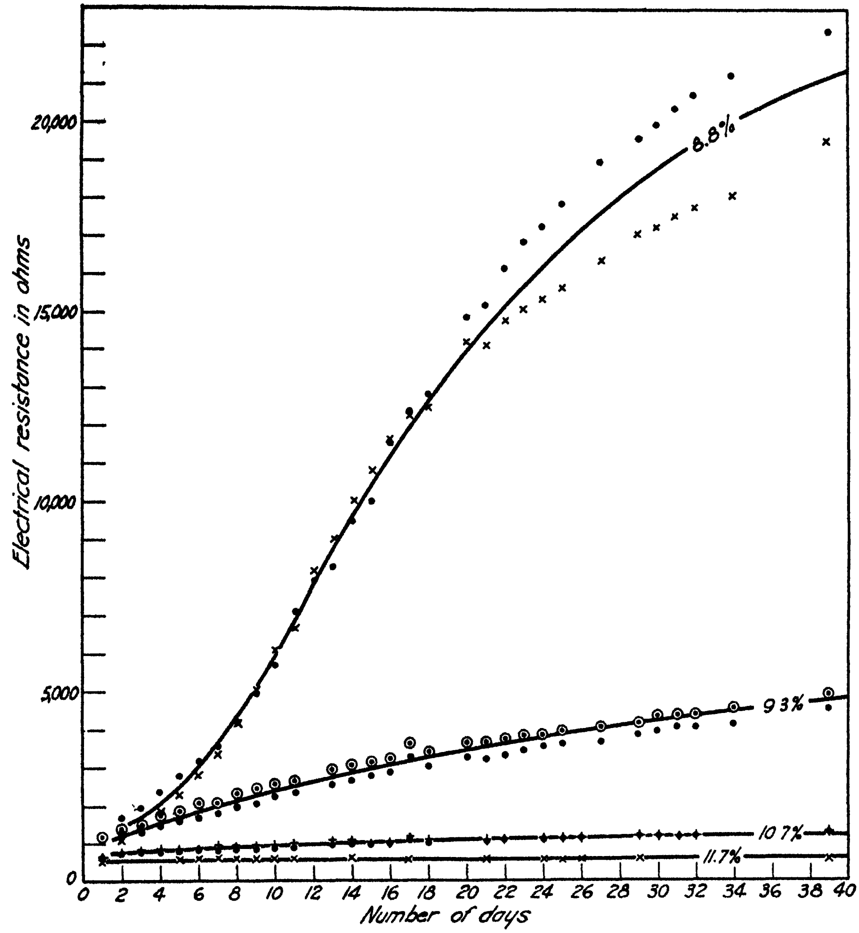

FIG. 2. DEPENDENCE OF THE 2-ELECTRODE PLASTER OF PARIS BLOCK RESISTANCE ON TIME AFTER BLOCK HAD BEEN PLACED IN A LARGE BODY OF YOLO FINE SANDY LOAM AT THE UNIFORM MOISTURE CONTENTS INDICATED

The results of two blocks, indicated by different symbols, at each of four different soil-moisture contents, are shown.

rounded by soil the moisture content of which is in the lower quarter of the range of available moisture to plants. The drier the soil, the more pronounced is the lag. The resistance is still rising rapidly after 40 days, for soil approximately 0.5 per cent above the permanent wilting percentage. A similar behavior is noted in figure 3 for the 4-electrode blocks, indicating that the lag is due entirely to the slowness of movement of the moisture at low moisture contents.

The location of the soil-moisture content of each curve of figure 2 is indicated by a dotted vertical line in the lower curve of figure 4, which we believe to be the true calibration curve, obtained as we shall describe later, for the 2-electrode block. The resistances of the blocks at the end of 40 days, in figure 2, are indicated in figure 4 by crosses, which are still considerably below the curve. It is

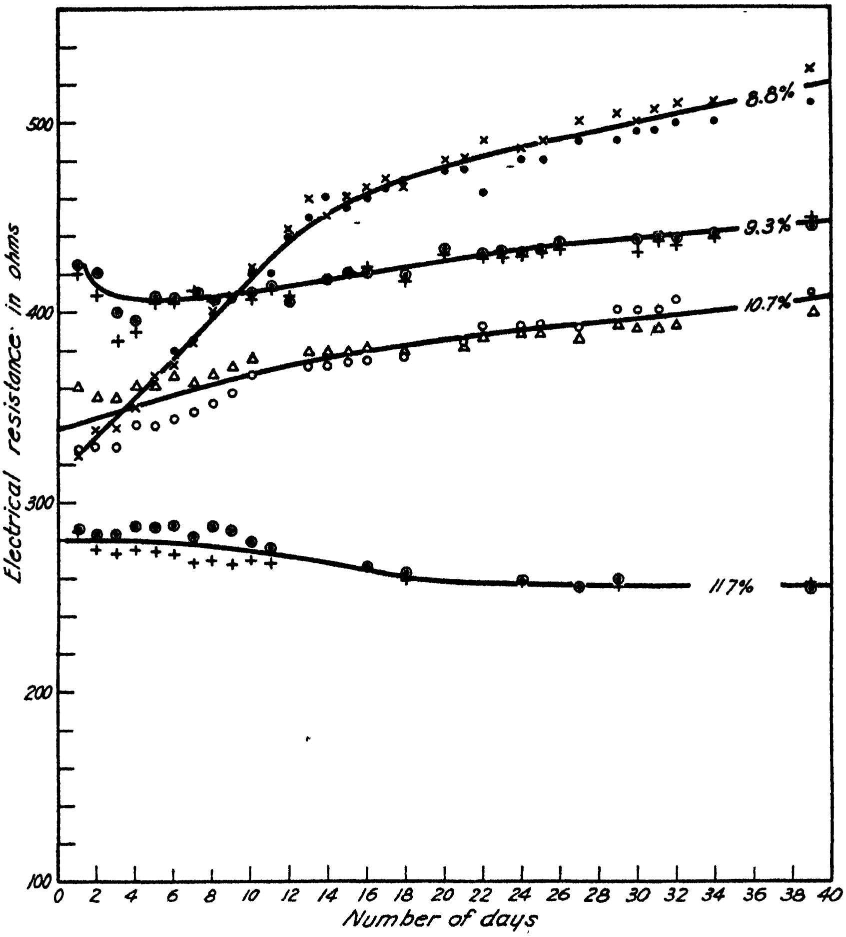

FIG. 3. DEPENDENCE OF THE 4-ELECTRODE PLASTER OF PARIS BLOCK RESISTANCE ON TIME AFTER BLOCK HAD BEEN PLACED IN A LARGE BODY OF YOLO FINE SANDY LOAM AT THE UNIFORM MOISTURE CONTENTS INDICATED

The results of two blocks at each of four different moisture contents are shown

evident, therefore, that considerable error may be made in locating the calibration curve at the lower soil-moisture contents by a method such as the foregoing.

Figures 2, 3, and 4 indicate that when the soil-moisture content is at a value just above the permanent wilting percentage, several months might be required for the plaster of paris block to attain equilibrium with the surrounding soil and thus possess the resistance value indicated by the true calibration curve. In fact,

if the blocks showed this lag in response in soil where plants were growing and if the block were used as an indicator of when to irrigate, the plant would normally have died long before the resistance reading of the block indicated that the moisture content was near the permanent wilting percentage.

REPRODUCIBILITY OF BLOCK READINGS IN PLANT-BEARING SOIL

The lag in response of the blocks to changes of soil-moisture content when the roots of actively transpiring plants surrounded the blocks was next investigated. The same blocks were imbedded in the same buckets of soil in which now several sunflowers (which served to vary continuously the moisture content of the soil surrounding the blocks) were grown. Each cycle of events commencing with an irrigation in which the soil is saturated and ending with the soil at the permanent wilting percentage enables us to plot a curve showing the dependence of the resistance of a given block on soil-moisture content. The degree of coincidence of the curves, each obtained from a different cycle, is an excellent indication of the reproducibility in behavior as well as of the amount of reliance that can be placed on the block as an indicator of soil-moisture content in soils in which plants are growing.

The surface of the soil was covered by overlapping sheets of leadfoil, permitting irrigation of the soil without an appreciable loss of moisture by evaporation from the soil surface. Thus it was found that there was as dense a growth of roots on the surface of the soil as at a short distance below. The sunflowers were illuminated continuously by several lamps totaling about 15,000 watts and they were cooled by a fan to avoid leaf burns.

There were in all three buckets, each containing three growing sunflower plants and four blocks placed in a vertical position at varying distances from the bottom of the bucket. The presence of the plaster of paris blocks did not seem to affect the development of the roots, as the density of the roots seemed to be just as great adjacent to the block surface as a short distance away.

The soil in the buckets was irrigated so heavily at the beginning of each cycle that it became almost a heavy suspension. This was indicated by the fact that the moisture equivalent of the soil was 16.8 per cent and that enough water usually was added to raise the moisture content above 40 per cent by weight. The water used was moderately hard, containing about 250 p.p.m. of solids.

To obtain an indication of the lag in response of the blocks to changes of moisture content, the average rate of transpiration for each cycle was intentionally varied by changing the intensity of the illumination. After an irrigation, the plants were allowed to continue to remove water, while readings were taken until the plants were very much wilted and the stalks were drooping considerably. A new cycle then was started and the same procedure repeated. The average daily rate of transpiration for the different cycles in any given bucket varied widely, as shown in table 1.

Reproducibility of 2-electrode block resistances. The results of about a third of our replications are given here. The agreement among all is at least as good as those presented.

If the blocks show a lag in response to changes of soil-moisture content, the curve for any given cycle (showing the dependence of block resistance on soil-moisture content) should fall lower in the graph, the more rapid the rate of transpiration during that cycle. That there is a surprising absence of lag in response for the 2-electrode blocks is shown in figure 4. Each curve is a composite of at least nine or ten complete cycles, and each point is labeled according to the cycle in which it was obtained.

The data for the 2-electrode plaster of paris blocks were obtained by plotting the electrical resistance between electrodes 1–2 as well as between 3–4 of a 4-electrode plaster of paris block. Because of block-symmetry, it is, of course, immaterial from which end of the block we begin to number. The important thing is that the curves represent the electrical resistance between the two sets of outer electrodes of the 4-electrode blocks and should therefore all show the same behavior. The results of four sets of electrodes are plotted in figure 4, the origin of the ordinate of each curve (plotted logarithmically) being displaced vertically from the adjacent curve by 1000 ohms.

The moisture equivalent and permanent wilting percentage of the soil are indicated by two vertical lines, thus showing, as has been pointed out elsewhere

TABLE 1

Average rate of transpiration during the different cycles

Cycle number	1	2	3	4	5	6	7	8	9
Length of cycle ... *days*	6	4	5	8	10	8	8	9	8
Daily transpiration or loss of water from soil in bucket ... *gm.*	310	537	418	279	303	443	365	260	365

(1), that the entire variation of the block resistance shown, occurs over the range of soil-moisture content of greatest importance to growing plants. For the plaster of paris blocks used, the figures show that the electrical resistance corresponding to the permanent wilting percentage is around 200,000 ohms; that corresponding to the moisture equivalent, around 500 to 600 ohms.

The curves of figure 4 are all approximately horizontal from the moisture equivalent to almost three times the latter value. The soil-moisture content at the beginning of the horizontal part of the curve doubtless corresponds to the minimum at which all of the pores of the plaster of paris block are entirely filled. Up to this point, the resistance decreases with increase of water in the block, but when the block is saturated, any additional water given to the soil cannot alter the observed electrical properties of the block in the soil, since the block is the locale of virtually all the current flow between the electrodes.

Reproducibility of 4-electrode block resistances. The results from the 4-electrode resistances are plotted in figure 5. These, like those of the 2-electrode resistances, show an excellent superposition in the loci of the points of the different cycles and therefore a total absence of lag in response of the blocks to changes of soil-moisture content. The value of the ordinate of each point was calculated, from four sets of virtually simultaneous resistance measurements made on each block, according to equation 2. The 4-electrode resistance measures only the

resistance of the medium in which the electrodes are embedded and is totally independent of any contact resistance between the plaster of paris and the electrodes. This, of course, is not true of the 2-electrode block, where the

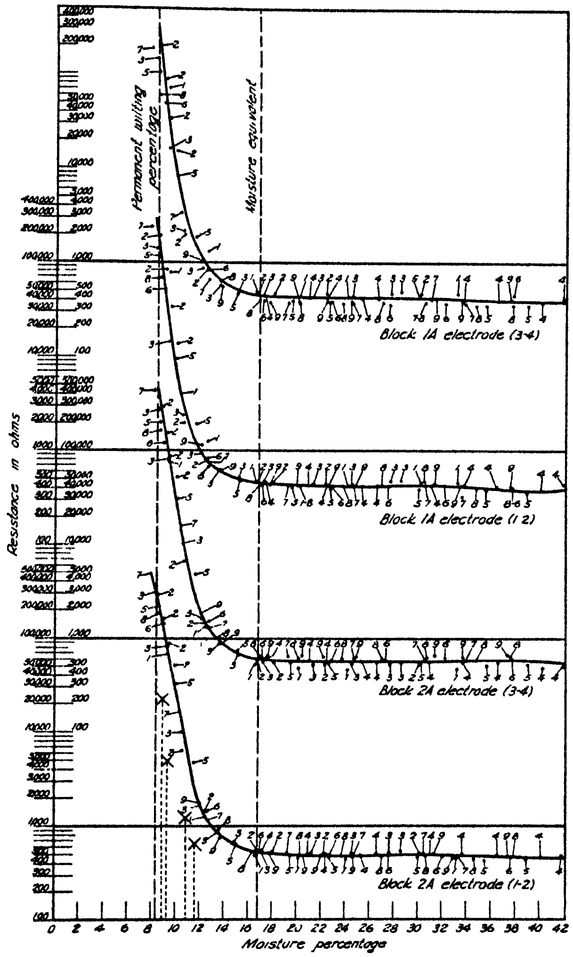

FIG. 4. CALIBRATION CURVES OF FOUR 2-ELECTRODE PLASTER OF PARIS BLOCKS PLACED IN YOLO FINE SANDY LOAM

Staggered vertical logarithmic scales indicate a displacement of the origins of adjacent curves by 1000 ohms. Number attached to each point indicates the number of the cycle during which the point was obtained. Each curve is the result of nine cycles of complete soil saturation and drying caused by growing plants.

measured value of the resistance is composed of the resistance of the medium together with two contact resistances.

There is a considerable resemblance in the shape of the 2-electrode and the 4-electrode curves except over the range of soil-moisture content above the moisture equivalent. In the first case, the curve is horizontal over this range and,

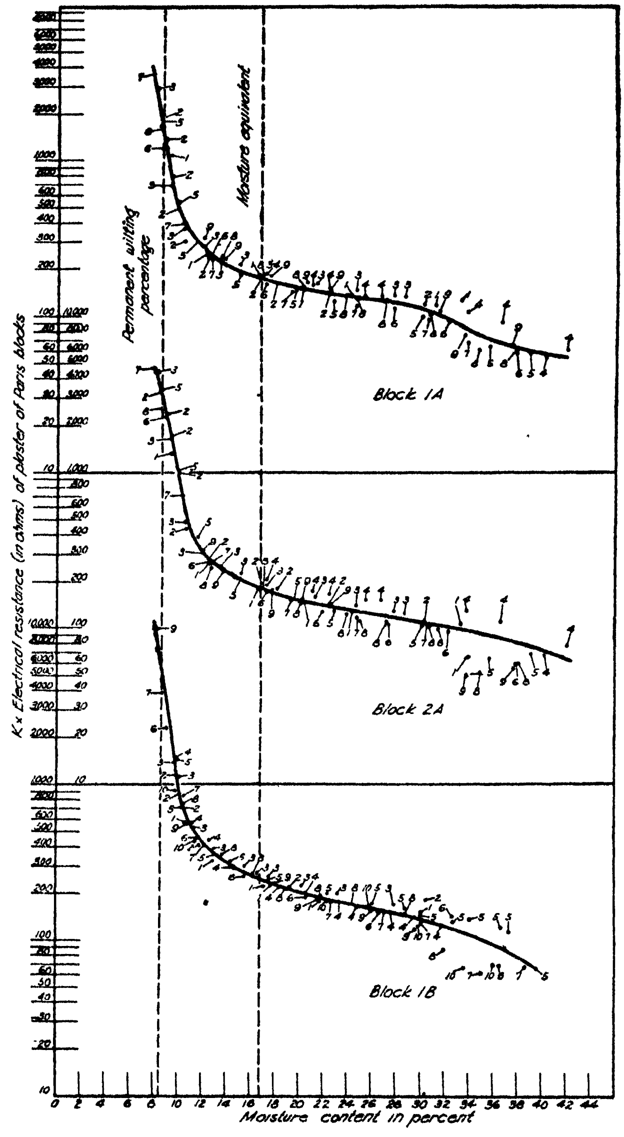

FIG. 5. CALIBRATION CURVES OF THREE 4-ELECTRODE PLASTER OF PARIS BLOCKS PLACED IN YOLO FINE SANDY LOAM

Staggered vertical logarithmic scales indicate a displacement of the origins of adjacent curves by 1000 ohms. Number attached to each point indicates the number of the cycle during which the point was obtained. Each curve is the result of nine or ten cycles of complete soil saturation and drying caused by growing plants.

therefore, the resistance is independent of soil-moisture content. In the second case, it continues to decrease considerably with increase of soil-moisture content.

The continued drop in resistance of the 4-electrode block with increase of soil-moisture content seems a bit startling at first when we recall that the 4-electrode

resistance measures only the resistance of the medium surrounding the electrodes, and that the resistance of the blocks should be constant above the moisture equivalent, since, as has been pointed out, the block is then saturated and its electrical characteristics should therefore be no further altered by an increase in the moisture content of the soil surrounding it.

A probable explanation of this anomaly is found if we consider figure 6. When we determine the resistance across electrodes 1–2, the lines of current-flow have a shape approximating the curved lines joining points 1–2. On the other hand, the lines of flow between electrodes 1–3 have a shape approximating the lines joining points 1–3. In the first case, a relatively large fraction, and in the second case, a relatively small fraction, of the lines of flow lie within the block. Since the resistance across either of the pair of terminals is determined by the resistance at each point in the medium traversed by the lines of current-flow, we see

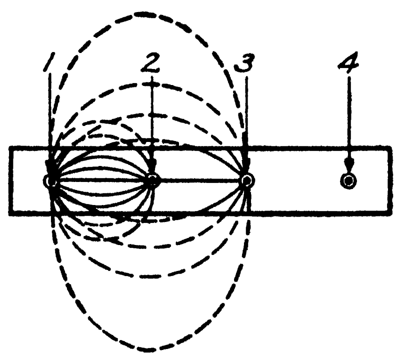

FIG. 6. SCHEMATIC REPRESENTATION OF LINES OF CURRENT-FLOW BETWEEN ELECTRODES OF A 4-ELECTRODE PLASTER OF PARIS BLOCK

that the resistance between electrodes 1–3 is very much more affected by the resistance of the moist soil surrounding the block than is that between 1–2.

Because of the horizontal nature of the curves above the moisture equivalent in figure 4 it seems likely that virtually none of the lines of current-flow between electrodes 1–2 pass out of the block into the surrounding medium. Once the block is saturated, its electrical properties remain unchanged with any additional increase in moisture content of the surrounding soil.

On the other hand, a much greater fraction of the lines of current-flow connecting 1–3 than of those connecting 1–2 should pass out of the block into the surrounding soil.[1] Any increase in the soil-moisture content will decrease the resistance along the lines of current-flow passing out of the block and traversing the soil. This will entail a decrease in the total resistance between 1–3. Thus we should expect the resistance between 1–3 to decrease with respect to that between 1–2 when the soil-moisture content is increased above the moisture equivalent. That this is the case is shown by figure 7. These curves represent the resistance between electrodes 1–3 and 2–4 of the blocks in bucket A. The

[1] Unpublished data indicate that this soil becomes saturated at a moisture content around 38 per cent. Beyond this it becomes a suspension.

resistance between 1–3 and 2–4 should, of course, behave alike because of symmetry.

Since the 4-electrode resistance μ_1 is given by the difference $(R_2 + R_5) - (R_1 + R_6)$, and since R_1 and R_6 correspond to the resistances between 1–2 and 3–4,

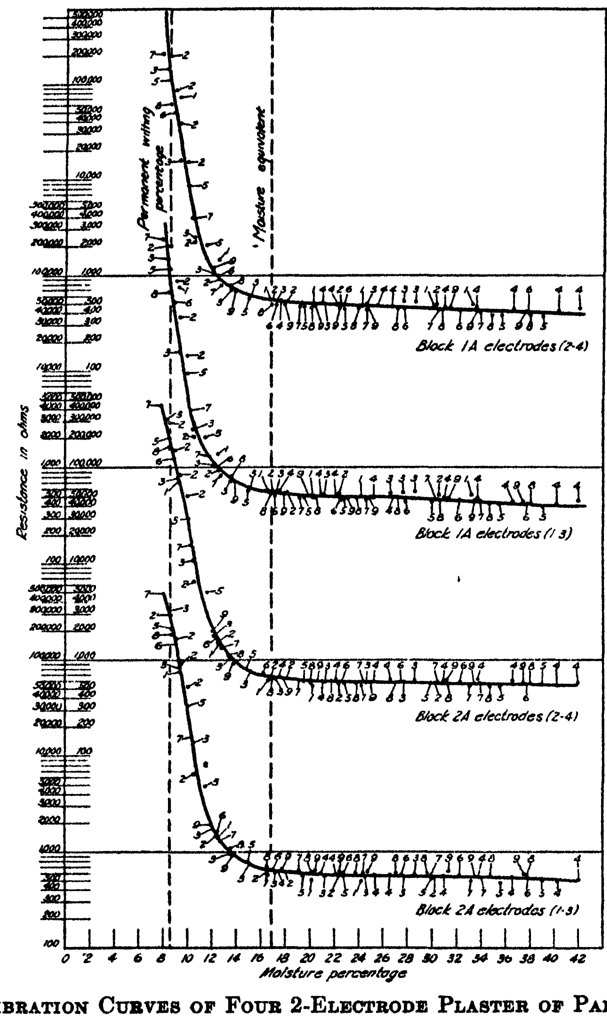

FIG. 7. CALIBRATION CURVES OF FOUR 2-ELECTRODE PLASTER OF PARIS BLOCKS THE ELECTRODES OF WHICH ARE TWICE AS FAR APART IN THE SAME BLOCK AS THOSE FROM WHICH FIGURE 4 WAS OBTAINED

and R_2 and R_5 correspond to those between 1–3 and 2–4, we should expect, although the block is saturated, that μ_1 will always decrease with increase of soil-moisture content as shown by figure 5.

The apparent similarity in shape of the 4-electrode to the 2-electrode resistance curves at the lower soil-moisture contents shows that a variable contact resistance between electrode and plaster of paris has no appreciable effect on the

characteristics of the 2-electrode resistance. The 4-electrode resistance, μ_1, which is independent of contact resistance, shows the same rapid increase with decrease of soil moisture as does the 2-electrode resistance, which includes two contact resistances.

BEHAVIOR-DISCREPANCY OF BLOCKS IN SOILS WITH AND WITHOUT GROWING PLANTS

The question still to be answered is: Why, where plants are growing, do we get such smooth and reproducible results over and over again as those shown by figures 4 and 5 even at the low soil-moisture contents; yet, where no plants are growing (figs. 2 and 3), more than a month is required for the block to acquire moisture equilibrium with the soil surrounding it?

Let us, for purposes of argument, consider the data from table 1. With so great a lag as that shown by figures 2 and 3 we should expect in figures 4 and 5 that the set of points associated with cycles 2 and 6, where the rate of transpiration according to table 1 averaged 490 cc. per day, should fall considerably below the set of points associated with cycles 4 and 8, where the transpiration averaged 269 cc. This follows because the smaller the rate of transpiration, the more time is allowed for the blocks to acquire, in an asymptotic way, the high equilibrium resistance. No such separation of the sets of points associated with the different cycles is observed in figures 4 and 5. In fact, the blocks in the buckets with the growing sunflowers seem to respond almost instantaneously to changes of soil-moisture content. Why, at soil-moisture contents near the permanent wilting percentage, do the blocks respond seemingly instantaneously in one case and infinitely slowly in the other?

The answer lies undoubtedly in the fact that in the soil where plants are growing, a very steep soil-moisture content gradient is developed and maintained in the boundary layer surrounding the block, whereas in the soil where no plants are growing, only a very small soil-moisture content gradient is developed. In the first case, the roots of the plant grow up to the face of the plaster of paris block, keeping the entire body of the soil, even up to the soil-block boundary, more or less at the same moisture content, thus maintaining a steep moisture-content gradient between the plaster of paris and the soil at the block bounadry. In the second case, a layer of soil of varying thickness surrounds the block. In it the soil-moisture content changes gradually from that at equilibrium with the block at the soil-block boundary, to that at equilibrium with the main body of the soil at a considerable distance from the boundary, thus furnishing a very small soil-moisture-content gradient. Now, since the rate of movement of moisture at any point is proportional to the gradient of the moisture content, the movement out of the block in the first case should be rapid; in the second case, very slow.

From the above, it clearly follows that the plaster of paris blocks, particularly at the lower soil-moisture contents in the vicinity of the permanent wilting percentage, should not be calibrated by embedding them in a representative sample of soil, then determining the equilibrium resistance of the block and finally the

moisture content of the soil surrounding the block. Our present evidence indicates though, that the block may be reliably calibrated by determining the relation between the resistance and the soil-moisture content, the latter being changed by thoroughly permeating roots of actively transpiring plants in the soil surrounding the block. The calibration should never begin until the roots of the plants have had time to permeate the soil surrounding the block. Also, it should preferably be carried out in a constant temperature tank since, as has been shown elsewhere (1), the resistance of the blocks depends upon the temperature.

DEPENDENCE OF 2-ELECTRODE RESISTANCE ON THE VARIATION OF ELECTRODE-SEPARATION

A comparison of the curves of figure 7, which were obtained from electrodes twice as far apart as those of figure 4, will show that there is a consistent difference between them but that this difference is small. This disagrees with conclusions drawn elsewhere (1) that the distance between the electrodes is important in fixing the resistance of the block.

The slight dependence of the resistance of the 2-electrode block on the separation of the electrodes is important in the manufacture of the blocks. The less the dependence, the less care is required in the proper spacing of the electrodes in order to make the results from the blocks comparable, and therefore the lower is the cost of their manufacture.

Theoretical considerations also support the fact that the dependence is relatively small. Consider the formula for the resistance μ per unit length between two straight parallel cylindrical electrodes (5, pp. 350–352), of radii a and b, placed with their centers at a great distance ρ apart in an infinite conducting medium. The formula is

$$\mu = \frac{\tau}{2\pi} \frac{\rho^2}{ab} \tag{3}$$

where τ is the specific resistance of the medium. For all practical purposes the above conditions apply to the plaster of paris block. If the separation of the electrodes is changed from ρ_1 to ρ_2 we can set $\rho_2 = k\,\rho_1$, where k is a number such as to satisfy this equation. From the above we obtain the change in resistance $\Delta\mu$ caused by the change in separation of the electrodes from ρ_1 to ρ_2

$$\Delta\mu = \mu_2 - \mu_1 = \frac{\tau}{2} \ln \frac{\rho_2}{\rho_1} = \frac{\tau}{\pi} \ln k$$

According to the dimensions of the 2-electrode plaster of paris blocks, which are essentially the same as those of Bouyoucos, we have $a = b = 0.032$ cm., $\rho_1 = 2.00$ cm., and therefore $\mu_1 = 4.13\,\frac{\tau}{\pi}$. The percentage change in resistance caused by a separation of the electrodes from ρ_1 to ρ_2 is then

$$\frac{\Delta\mu}{\mu} 100 = 24.2 \ln k = 65.4 \log k \tag{4}$$

If now the separation of the electrodes is doubled by going from that corresponding to figure 4 to that corresponding to figure 7, $k = 2$ and the percentage change is

$$\frac{\Delta\mu}{\mu} 100 = 19.6 \text{ per cent}$$

This, as a matter of fact, is approximately the amount by which the resistances of figure 7 are greater than those of figure 4 at the same moisture contents.

Let us apply equation 4 to the practical case of finding what change in the resistance of the 2-electrode block is caused by the error of placing the electrodes 2.30 cm. instead of 2.00 cm. apart. Then k is 1.15 and

$$\frac{\Delta\mu}{\mu} 100 = 4.0 \text{ per cent}$$

If we had accidently placed the electrodes 1.70 cm. instead of 2.00 cm. apart k would be 0.85 and the error would be

$$\frac{\Delta\mu}{\mu} 100 = -4.85 \text{ per cent}$$

Thus an error of 15.0 per cent in the distance of separation of the electrodes during the casting of the block should cause only a change of about 4.5 per cent in the resistance readings of the block. These theoretical considerations show that for all practical purposes not an excessive amount of care need be exercised in the spacing of the electrodes in the midplane of the block, as long as their separation falls around 2.00 cm.

SUMMARY

Laboratory investigations of the 2- and 4-electrode plaster of paris block show that:

The blocks can be calibrated at all moisture contents by placing them in a soil surrounded by the roots of actively transpiring plants and then observing the relation between soil-moisture content and block resistance. Because of the tremendous lag in response shown by the block to the value of the moisture content of soil in which no plants are growing, the blocks cannot be calibrated satisfactorily in the absence of roots of actively transpiring plants at the lower ranges of soil-moisture content.

Both the 2- and 4-electrode plaster of paris blocks, the preparation of which is described, show a remarkably reproducible behavior in that, under like soil-moisture contents in the soil tested, the blocks always possess a like resistance at all soil-moisture contents extending from the permanent wilting percentage to almost three times the moisture equivalent.

Over the entire range of readily available moisture to plants, both the 2- and 4-electrode plaster of paris blocks will serve as dependable and practical indicators of the soil-moisture content of any locality in a body of soil where the blocks can be buried and where the changes in soil-moisture content are caused by the removal of the moisture by the roots of actively transpiring plants. As a soil-

moisture content indicator, the 2-electrode is better than the 4-electrode block because of the simplicity in the manufacture and in the measurement of the resistance.

The 2-electrode resistance of a plaster of paris block is not very sensitive to variations in the separation of the two electrodes in the midplane of the block.

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AN AUTOMATIC SELF-RECORDING INFILTROMETER[1]

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Infiltration as one of the major phases of the hydrologic cycle has been studied by numerous investigators. The various types of devices used for this purpose have been grouped and discussed in a previous paper[3]. It is the writers' conviction that data on true areal infiltration can be obtained only by means of run-off measurements from natural watersheds. Even there, absolute data are not always easily obtained, as evaporation, transpiration, interception, surface detention, and ground-water outflow modify the fundamental formula: infiltration equals rainfall minus run-off. The value of any mechanical device for the determination of areal infiltration capacities remains problematic. Lateral subsurface flow may remove water beyond the plot boundaries, without corresponding accretion of such water from outside the plot. On the other hand, the drier soil surrounding the plot allows the soil air to escape laterally, whereas during a natural rain the confined soil air forms an impediment to the entrance of water.

Nevertheless, infiltrometers are essential tools in hydrologic research, as they allow the study of relative infiltration capacities of soils. Infiltrometers lend themselves well to the study of the effect of various treatments upon the hydrologic properties of soils. Such tests can be carried out on small plot experiments where it is impossible to obtain the same information by the measurement of rainfall and run-off. Moreover, infiltrometers can be used to provide a volume of data in a short time and independently of weather conditions, whereas rains producing run-off are infrequent.

An automatic self-recording infiltrometer, devised in 1940 and operated during 1941, has proved to be a convenient and efficient instrument for obtaining relative infiltration data. The purpose of the use of infiltrometers in connection with the Indiana agricultural hydrologic studies is to identify superior methods of soil management in order that such methods may be applied on experimental watersheds, where their moisture-conserving and erosion-resisting properties will be tested under natural conditions in comparison with similar tests of prevailing farming practices.

Originally the Coshocton grid-type infiltrometer was used for these studies[4].

[1] Contribution from the Soil Conservation Service cooperating with the Purdue Agricultural Experiment Station, Lafayette, Indiana. Journal Paper Number 12 of the Purdue Agricultural Experiment Station.

[2] Assistant agricultural aide and associate soil scientist, respectively. The authors wish to express their appreciation for assistance and advice rendered by R. B. Hickok, project supervisor, Soil Conservation Service, Lafayette, Indiana.

[3] KOHNKE, H. 1938 A method for studying infiltration. *Soil Sci. Soc. Amer. Proc.* 3: 296–303.

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It was later modified to make the outflow of water automatic by closing the burettes on top and placing the outlet rubber tube close to the surface of the ground so that water could flow only when the level of the water on the ground was low enough to allow air to enter the burette. This is a technique previously described by Musgrave[5]. As the capacity of the burettes corresponded merely to ¼ inch of water on the ground, constant attention and frequent refills were necessary.

DESCRIPTION OF THE AUTOMATIC SELF-RECORDING INFILTROMETER

In order to simplify the experiments and to obtain continuous records of the rate of infiltration, an automatic self-recording infiltrometer was devised (figs. 1 and 2). Water is applied to the ground from a tank which rests on the balance of a recording rain gage (Friez, model #6912, reconnaissance rain and snow gage). The water passes through a rubber hose to a plot which is enclosed by a steel frame 3 inches high, half of which is driven into the ground to check surface run-off. The decrease in weight of the tank, representing the infiltration that

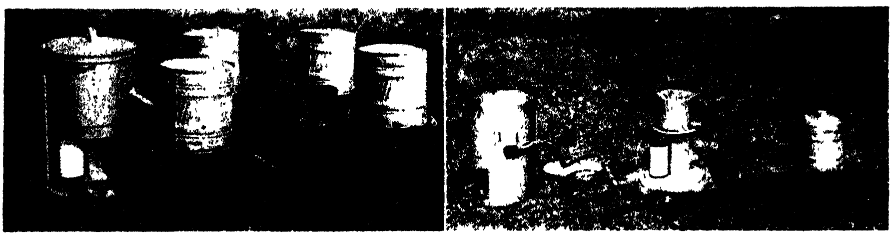


FIG. 1 FIG. 2

FIG. 1. ASSEMBLED APPARATUS IN OPERATION
FIG. 2. DISASSEMBLED APPARATUS, SHOWING COMPONENT PARTS

has occurred, is recorded on the chart of the revolving clock drum. The area to which water is applied from the tank is a square 7.09 inches on the side, the same as that of the 8.00-inch-diameter rain-gage catchment, so that gage readings are direct in inches of infiltration. In order to decrease lateral water movement in the soil, four buffer compartments are placed around the central plot. The steel frames of the inside and the four outside compartments consist of five individual units that can be pressed into the ground easily. The buffer compartments are fed by 3-gallon tanks. No continuous records are kept on the rate of infiltration of the outside plots; merely the total infiltration is determined by the difference in weight at the beginning and at the end of the experiment. Each rectangular buffer plot, 5.5 by 12.6 inches, has an area 1.38 times that of the center plot. The change of weight of the outside tanks in pounds times 0.4 corresponds to the amount of infiltration in inches. The capacity of the central container corresponds to 6 inches of water on the ground, whereas the capacity of the outside tanks corresponds to 10 inches; thus, infiltration normally continues on the buffer plots after it has ceased on the central plot.

[5] MUSGRAVE, G. W. 1936 The infiltration capacity of soils in relation to the control of surface run-off and erosion. *Jour. Amer. Soc. Agron.* 28: 727–739.

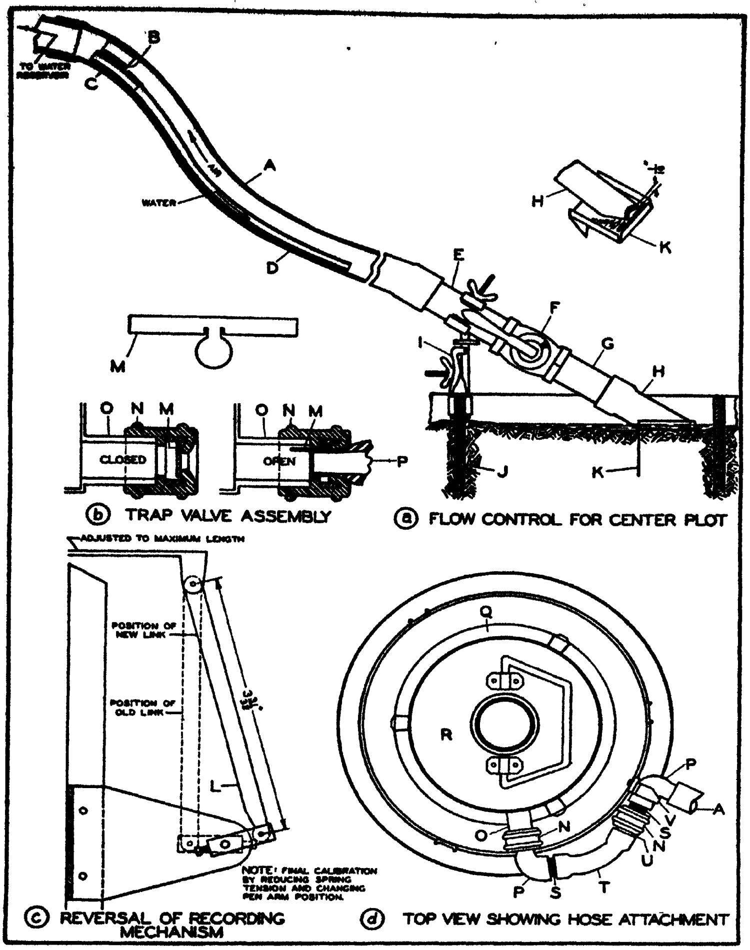
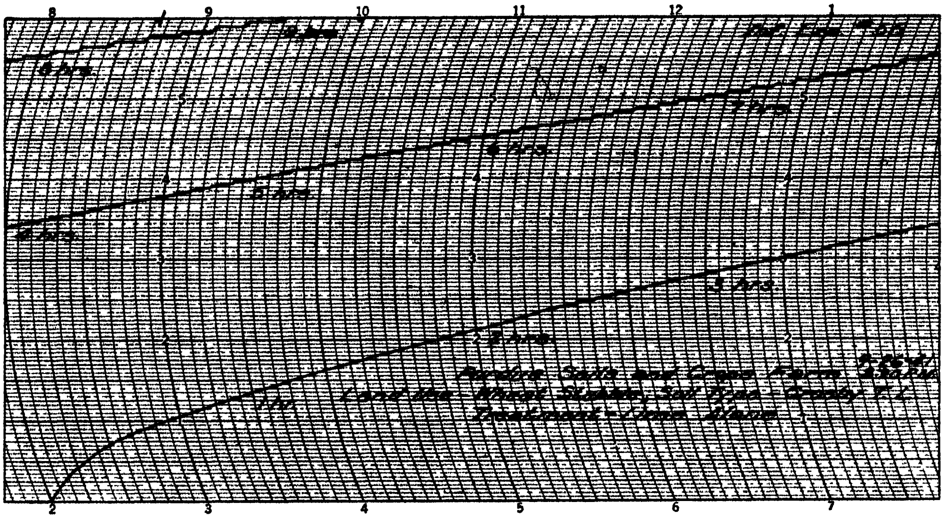


FIG. 3. DETAILS OF ESSENTIAL PARTS OF INFILTROMETER

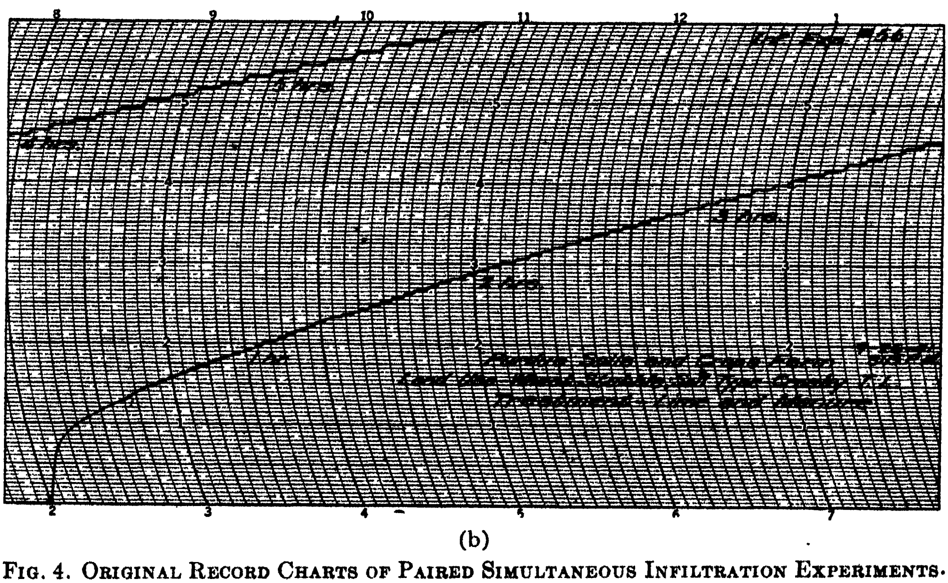
Parts list

SYMBOL	PART	SPECIFICATIONS
A	Rubber tubing	24″ × 3/8″ I.D. × 1/8″ wall
B	Two-hole rubber stopper	Stopper #2; 1/4″ holes
C	Brass tubing	1½″ × ¼″ dia.
D	Rubber tubing	10″ × 3/16″ I.D. × 3/32″ wall
E	Galv. W. I. pipe, one end threaded	3½″ × ½″ I.P.S.
F	Brass straight way stopcock-lever handle	½″ I.P.S.
G	Galv. W. I. pipe, one end threaded	2½″ × ½″ I.P.S.
H	Rubber tubing cut slantwise at outlet	2½″ × 5/8″ I.D. × 1/8″ wall
I	Placement clamps	Parts of two burette clamps
J	Ground compartment walls	3″ × 1/8″ thickness S.A.E. tool steel; heat treated (see text for plot dimensions)
K	Water stilling plate	1½″ × 1½″ surface
L	New vertical link	4½″ × ¼″ × 1/16″
M	Rubber valve	2¼″ × ¼″ × 1/16″; ½″ circular flap
N	Faucet connection	Commercial "Faucet Queen"
O	Container outlet	1″ × 1″ dia.
P	Street elbow W.I. pipe fitting	½″; male threads removed
Q	Balance platform	....
R	Water container	6½″ × 8″ I. D.
S	Galv. W.I. pipe; threaded one end	1″ × ½″ I.P.S.
T	Rubber tubing	3½″ × 5/8″ I.D. × 1/8″ wall
U	Tapered metal tube	1½″; dia. from 5/8″ to ½″; 1/32″ thickness
V	Metal clamp	....

Figure 3a demonstrates the construction of the water hose, which contains an inside tube to allow water to flow out while air passes upward. This device is necessary to decrease the amount of water released, each time air enters the



(a)



(b)

FIG. 4. ORIGINAL RECORD CHARTS OF PAIRED SIMULTANEOUS INFILTRATION EXPERIMENTS. TREATMENTS FROM 1917 TO 1941: (a) LIME ALONE; (b) LIME AND MANURE

system. It thus ensures a more uniform level of water on the ground and a smoother record.

To prevent its weight from affecting the operation of the balance, the water hose is attached to the side of the infiltrometer. A horizontal rubber tube

section with flexible connections carries the water from the central container to this point (fig. 3d). To permit the removal of the central tank from the balance while refilling, a trap valve connection is installed at the tank outlet (fig. 3b).

When the gage is used for its original purpose, the rain increases the weight of the bucket; when it is used as an infiltrometer, the weight of the container decreases as infiltration goes on. This results in a change in direction of the recorder pen. In order to make direct records possible on the ordinary chart paper, the operation of the recorder pen is reversed (fig. 3c).

For satisfactory operation, the infiltrometer must be placed level. This can be facilitated by the installation of spirit levels and leveling screws.

DISCUSSION OF THE APPARATUS

The handling of the automatic self-recording infiltrometer is very simple. One person can easily handle two outfits simultaneously, including the hauling of water. Depending on the desired duration of the runs and the number of supplementary soil determinations required, two or three pairs of experiments can be carried out within 24 hours. One of the advantages of this apparatus is the possibility of continuous operation.

As has been pointed out, no absolute infiltration values corresponding directly to conditions of a natural watershed are expected with this or any other infiltrometer of limited size. In order to obtain useful information concerning infiltration, a comparison between two types of conditions is necessary. Two infiltration experiments, therefore, are run simultaneously on two neighboring locations that vary in soil type, treatment, or vegetation. In this way time, which, because of atmospheric conditions, may have a great effect on infiltration, is eliminated as a variable. Figures 4a and 4b show typical data on the original record charts of two simultaneous infiltration experiments.

In order to facilitate an evaluation of the automatic self-recording infiltrometer, its advantages and disadvantages are enumerated, as follows:

Advantages

A continuous record of infiltration is obtained, showing any change of rate when it occurs.

This record is obtained automatically, and is not subject to errors of the operator.

The infiltration run can be extended over several hours, or until 6 inches of water have been applied.

Many experiments can be performed in a relatively short time, allowing study simultaneously of the infiltration rate of two similar sites that differ essentially only in one plant or soil factor.

The operation is simple.

The expenses for procurement and operation are low in comparison with those for the sprinkler-type infiltrometers. For the transportation of two outfits and the necessary water a half-ton pickup truck suffices.

Limitations

The area of the infiltration plot is small; therefore, sideward movement of water and air in the soil may tend to increase in filtration rates. (This effect is partly compensated by buffer plots.)

No attempt is made to simulate natural rainfall.

THE THERMAL CONDUCTIVITY OF DRY SOIL

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Several studies (8, 9, 10) of thermal transfer in soils have been summarized by Baver (1). These investigations have dealt primarily with thoroughly dried, crushed, sieved, and repacked soil materials in which the natural arrangement of the soils was completely altered. Such a treatment of the soil is necessarily accompanied by disintegration of the natural soil aggregates; hence the original pattern of soil porosity and the character of the natural soil structure, which condition the flow and transfer of heat through the soil, have been changed materially. It is doubtful, therefore, if the data of the earlier investigations, although complete for artificially packed soil materials, are sufficient for determination of the thermal conductivity of natural soil. For this reason it is desirable to compare the heat conductivity of various undisturbed soils with that of their component materials subjected to the previously used mechanical treatment, including crushing and sieving.

Investigation of this kind is important, not merely because it may demonstrate the difference in thermal transfer in a virgin soil and in the mechanically rearranged material of such a soil, but also because it may reveal certain fundamental facts about the heat flow in these two media, which must be considered in practical agriculture.

Cultivation of the virgin soils for preparation of suitable seedbeds may be roughly compared with a laboratory treatment of soil samples. It alters, although perhaps less drastically, the actual arrangement of the soil particles and structural aggregates, as well as the soil consistency and the pattern of soil porosity. Obviously it changes the condition of heat transfer. In order to understand, to evaluate, and to control the character and extent of such changes, one must know the fundamental facts underlying the physical behavior of the original medium which is to be subjected to modification, for then only can the effects of treatment be adequately predicted.

Germination of seed, root development, and growth of the plant depend upon the conditions of the soil, including its chemical composition and physical properties. The native plants, perhaps, are properly adjusted to the set of conditions developed by the virgin soil. The introduced crop plants, however, may need an altered soil. A modification of certain unfavorable conditions such as, for example, an exceedingly compact consistency, and preservation of others, such as specific types of soil structure, may be required. This investigation is concerned with the thermal factor, and the emphasis is on the influence of various types of soil structure upon the transfer of heat in the soil.

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SOILS STUDIED

In this study three soil types were used; namely, Miami silt loam from Wayne County, Indiana; Miami silty clay loam from Lenawee County, Michigan; and Chester loam from Montgomery County, Maryland. Miami silt loam is a normal gray-brown podzolic soil developed from calacareous drifts from the Late Wisconsin glaciation. Miami silty clay loam is similar to Miami silt loam in general characteristics. It is, however, noticeably heavier in texture throughout, particularly the B horizon. The parent glacial till contains more shale and its weathered products than the till usually underlying the Miami soils. Chester loam is a normally developed soil of the northern part of the Piedmont plateau derived from the weathered products of gneiss and granite.

Monolithic samples from different horizons of each of these soils were collected.[2] For the purposes of description Nikiforoff's classification and nomenclature (7) of soil structure is used since it lends itself readily to the theoretical developments later in this paper.

The profile of Miami silty clay loam is represented by the following samples (laboratory number, horizon, depth from the surface soil, and abbreviated description):[3]

C6615—A_1, 0–4 inches. Very dark brownish-gray silt loam with weakly developed fine granular structure.

C6616—A_3, 4–9 inches. Light yellowish-gray silt loam with moderately developed medium platy structure.

C6617—B_2, 11–16 inches. Yellowish-brown heavy silty clay loam with well-developed medium blocky structure.

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[2] The sample of Miami silty clay loam was collected by James Thorp, James K. Ableiter, and M. Striker, of the Division of Soil Survey, Bureau of Plant Industry, and the writer. The sample of Miami silt loam was collected by Thorp and the writer. The sample of Chester loam was collected by C. C. Nikiforoff, of the Division of Soil Survey, H. G. Byers, of the Division of Soil and Fertilizer Investigations, and the writer, from a location selected by W. E. Hearn, Division of Soil Survey.

[3] The complete description of Miami silty clay loam (by Thorp) is as follows:

C6615-A_1, 0-4 inches. Very dark brownish gray, slightly gritty and softly granular silt loam. Granules and crumbs partly angular and partly round and vary from 1 to 3 mm. in diameter. Lower part light colored.

C6616—A_3-B_1, transition 4–9 inches. Yellow or light brownish-yellow silt loam grading to light silty clay loam in lower part. Light yellowish-gray when dry. Lenticular aggregates in upper part 2 to 4 mm. thick grading downward to ill-defined medium nut-like aggregates.

C6617—B_2, 9–16 inches. Sample 11–16 inches. Yellowish-brown heavy silty clay loam with very distinct firm aggregates varying from $\frac{8}{16}$ to 2 cm. in diameter and having good breakage in two directions. Aggregates are subangular to sharply blocky in shape.

C6618—B_3, 16–30 inches. Sample from about 22–26 inches. Sharply blocky aggregagates with many faces and sharp corners 1 to $2\frac{1}{2}$ cm. The texture is silty clay loam. Aggregates thickly coated with dark brown sticky colloids.

C6619—C_1, 30–34 inches. Olive-drab silty loam till with much lime in crevices and disseminated. Horizontal breakage clearer than vertical. Aggregates sharply blocky and 1 to 3 cm. in diameter.

C6618—B_3, 22–26 inches. Dark-brown silty clay loam with well-developed medium blocky structure.

C6619—C_1, 30–34 inches. Olive-drab silty clay loam with moderately developed coarse blocky structure.

C6620—V_b, same as C9917 and C6618. Cut vertically from the B horizon, whereas all the rest of the samples were cut horizontally, i.e., parallel to the surface.

The samples of Miami silt loam are as follows:[4]

C6621—A_1, 0–2 inches. Medium gray silt loam with weakly developed medium granular structure.

C6622—A_2, 2–5 inches. Light gray silt loam with moderatly developed medium platy structure.

C6623—A_3, 5–11 inches. Light brownish-gray silt loam with poorly developed coarse platy structure.

C6624—B_2, 15–30 inches. Brown silty clay loam with moderately developed medium blocky structure.

C6625—B_3, 30–36 inches. Light brown clay loam with weakly developed coarse blocky structure.

C6626—C, below 36 inches. Light grayish-brown silty clay loam with poorly developed coarse blocky structure.

C6627—V_b, same as C6624 and C6625 but cut vertically from the B horizon.

The samples of Chester loam are these:[5]

C6628—A_2. Light brown loam with poorly developed medium granular structure.

C6629—B_2. Reddish brown clay loam with moderately developed medium blocky structure.

C6630—C. Light brown silt loam with poorly developed fine platy structure.

COLLECTION OF SAMPLES

Two different methods were used to collect these monolith samples, as follows:

The method illustrated in figure 1 was used to obtain the Miami samples. A column, *S*, of undisturbed soil, of square section 16 inches on a side and to the depth of the profile, was isolated by excavating the soil around it for a distance of 2 feet from its outer edges. The effect was a rectangular pit slightly over 5 feet square, with a column of undisturbed soil in its center. The shaft was then separated into sections, each of which included, for the most part, a single horizon. In addition, a vertical section, *T*, through the B horizon was obtained, in each of these profiles, from the outer wall of the excavation. The sections so obtained were wrapped in paraffin paper and sealed with a generous covering of liquid paraffin to prevent extensive evaporation. They were next supported with corrugated paper board and bound securely for shipment. Examination after reaching their destination showed no disturbances in the soils.

From each of these monoliths smaller undisturbed samples were cut in the laboratory and fitted into thoroughly paraffined wood frames having outside dimensions 8 by 8 by 1 inch and $\frac{3}{8}$ inch thick. The faces were carefully shaved by a draw shaver until flush with the edges of the frame. Thin hard-rubber plates, $\frac{1}{64}$ inch thick, were then placed over the soil surfaces and sealed to the frames. Duplicate samples, taken as close together as possible, consistent with clean separation of the two, were obtained from each 16-inch monolith sample. A single wood jig of square section, shown in figure 2, was used to sup-

[4] For a complete description of this soil see reference (4).

[5] For a complete description of this soil see reference (3).

port the sample when the second face was prepared. The jig slides, with close fit, over the wood frame, and leaves exposed the surface to be dressed. Two of these jigs, one on either side of the monolith and clamped together by bolts, were used to support the soil during separation of the duplicate samples. The initial thermal measurements of these smaller

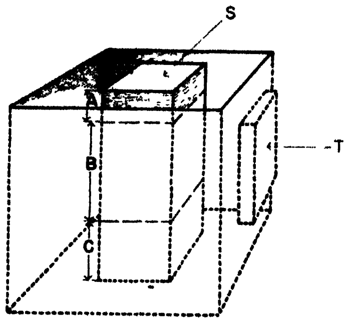

FIG. 1a. SCHEMATIC DRAWING OF METHOD USED TO OBTAIN SAMPLES OF MIAMI SOILS
The major soil horizons A, B, and C are shown. *S* is the column of soil to be sectioned. *T* represents a vertical section through the B horizon

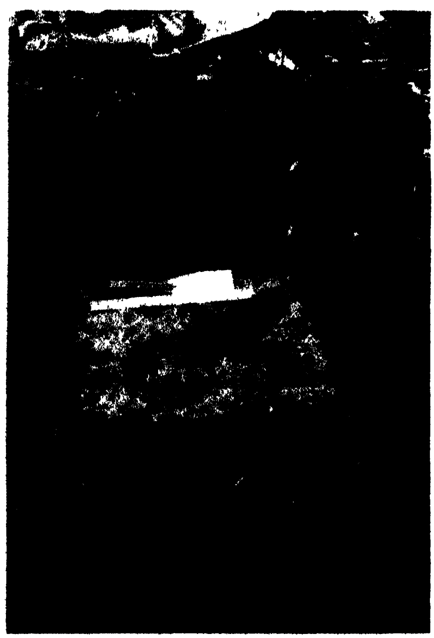

FIG. 1b. COLUMN SHOWN IN FIGURE 1a (MIAMI SILTY CLAY LOAM).
One corner of the soil column *S* remains fastened to the outer pit wall as successive sections are cut

samples were made with the moisture content as it existed at the time of final preparation, that is, when sealed within the wood frame.

A somewhat different procedure was used to obtain the Chester soil samples. These were prepared and fitted into final form entirely in the field with a specially designed die. A

large rectangular excavation about 5 by 3 feet was prepared. The samples were cut with the die and fitted into the wood frames directly from recessed shelves on the sides of the pit. In this way, it was possible to prepare the chosen samples of Chester loam, six in all, in little more than half a day.

The special die used is of steel and is illustrated in figure 3. *A* is a square die of the dimensions shown. It may be unfastened at two joints, *a* and *b*, and removed in two sections to avoid injury to the samples. The union is made by countersunk screws, *e*. The square wood frame *B* is supported on the top of the steel die *A* by four clips, *F*; these clips fit loosely into the lugs *C*, which are rigidly fixed to *A*. The yoke *D* fits over opposite pairs of clips and is used to drive or push the die and frame into the soil; by its use no force is applied

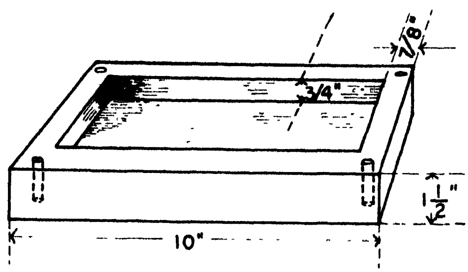

Fig. 2. Wood Jig Used for Final Preparation of Samples

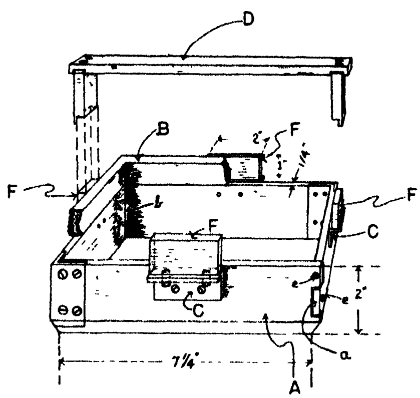

Fig. 3. Special Die Used in the Field to Cut Chester Soil Samples

to the wood frame *B*, but only on the steel die *A*. The inside dimensions of *A* and *B* are identical. Hence it is possible to push the frame *A* into the soil until the desired soil stratum fills the wood frame. The process is a gradual one, the die being driven but lightly and the soil cut from outside the die, as required for easy penetration and no disturbance of the natural structure within. Care must be taken to keep the wood frame in contact with the steel frame *A*. Auxiliary clips anchored rigidly on *A* and clamping on the upper edge of the wood frame, undoubtedly would be better suited to hold the latter in place.

After the wood frame *B* is filled, the top surface is carefully dressed with a draw shaver and made level with the frame. The hard-rubber cover is sealed on; thin cellophane tape is adequate for the purpose. The die and its burden are severed from the parent soil. A wood jig (fig. 2) is placed over the partly sealed wood frame for support, the sample is inverted, and the die *B* removed by unfastening the joints *a* and *b*. The second face, with the sample supported in the jig (fig. 2) is then dressed, and sealing completed.

EXPERIMENTAL PROCEDURE ON MONOLITH SAMPLES

The preparation and procedure in the laboratory were identical for all samples. The wet samples were weighed and the thermal conductivities measured in the moist state. The hard-rubber covers were unsealed and the samples allowed to become air-dry. An interval of not less than 2 weeks, during which the sample was inverted once, was allowed. Each sample, supported on its lower hard-rubber cover, was placed on a separate paper during drying, and all soil lost in the process was collected. No loss of more than 0.1 per cent of the dry weight was found in any case; for most, it was considerably less. The upper cover was removed completely to allow good contact with the air. Ventilation was possible since the lower cover was unsealed. The dimensions were measured and the approximate bulk shrinkage was calculated. This was small in all cases. When sufficiently dry, the face plates were resealed and the samples weighed. Thermal conductivities were then measured on the dried samples.

The apparatus used and the methods of measurement are fully described elsewhere (9, 10). The only modification required was the substitution of a wood container having hard-rubber face plates $\frac{1}{64}$ inch thick.[6] The face plates can be very slightly recessed, about 0.001 inch, for sealing with cellophane tape. The wood frames were thoroughly boiled in paraffin to render them moisture-proof. Samples were allowed to remain, under a thermal gradient, 24 hours, for the most part, until test measurements showed that equilibrium prevailed

CONDUCTION IN MONOLITH SAMPLES

Table 1 shows the thermal data for air-dry monolith samples. The designations are those ordinarily used on horizonal samples, except for C6620 and C6627 where V_B indicates a vertical section taken through the entire B horizon; the measured sample, however, did not include the whole of this horizon. The fourth column shows the observed thermal conductivities. The remaining columns show the porosity, volume weight, and textural density (true density of the soil particles).

The data on thermal conductivities of the crushed and sieved soil materials will be given in a following section of this paper. The data on heat transfer in the moist soils will be given in subsequent papers. The immediate discussion

[6] When thermal conduction measurements are made using as covers hard-rubber face plates, correction is required for the face-plate thickness. The following relation is easily derived and is sufficient:

$$k = d/[\{(A\delta t/Q\} - (2\tau/k')]$$

where k is the thermal conductivity of the soil, k' that of the face-plate material (0.000382 cal./cm. sec. deg. C. for hard rubber), τ is the thickness of the face plate, and d that of the soil, A is the area of measurement, Q the heat transmitted in unit time under a thermal gradient δt across the soil and face plates, by the area A when in the steady state (1, 9). An alternate procedure would be to place the thermocouples just under the face plates and in contact with the actual soil faces. δt would be the actual gradient across the soil, determined from these couples. The correction term $2\tau/k'$ is then not required and the equation $k = Qd/A\delta t$ suffices.

will be limited to the thermal relations of air-dry natural soils as represented by monolith samples. Moisture contents in these air-dried samples are too small to affect materially the thermal transfer.

The data in table 1 demonstrate that, ordinarily, soils having a low porosity are the best conductors, whereas the more open soils are the poorest conductors. Comparison of the data in table 1 with the data given elsewhere (9, table 1) on Kalkaska loamy sand shows that the conductivity of packed sand is much less than that of some undisturbed clay soils. For example, C3191, an artificially packed sand, has a porosity of 42.9 per cent and a thermal conductivity of 4.61 units, whereas C6617, which was cut from the clayey soil horizon, has a porosity of 33.3 per cent and a thermal conductivity of 8.06 units. This example illustrates the influence of porosity on thermal transfer in a soil.

TABLE 1

Summary of thermal data on air-dry monoliths

SAMPLE NUMBER	SOIL	HORIZON	THERMAL CONDUCTIVITY*	P POROSITY	v VOLUME WEIGHT	d DENSITY (SOLIDS)
				per cent	*gm./cc.*	*gm./cc.*
C6615	Miami silty clay loam	A_1	3.27	55.2	1.16	2.59
C6616		A_3	7.38	32.2	1 84	2 71
C6617		B_2	8 06	33 3	1.82	2.73
C6618		B_3	8 17	33 2	1 83	2.74
C6619		C	8 44	34.8	1 80	2.76
C6620		V_B	7.19	36.9	1.73	2.74
C6621	Miami silt loam	A_1	4.15	56.8	1 12	2.59
C6622		A_2	5 99	44.9	1 47	2 67
C6623		A_3	7.81	39 2	1.63	2 68
C6624		B_2	7 51	36.4	1.73	2 72
C6625		B_3	6 88	40 1	1 64	2.74
C6626		C	9.18	33.2	1.85	2 77
C6627		V_B	6.22	36.2	1.74	2.73
C6628	Chester loam	A_2	4.85	54 1	1 24	2.70
C6629		B_2	7.15	43 9	1.55	2.76
C6630		C	5.23	47.5	1 49	2 84

* 10^{-4} cal./cm. sec. deg. C.

Further examination of table 1 shows that the relation of thermal conductivity to porosity is not generally so simple as the examples of the preceding paragraph might indicate. Samples C6620 and C6629 have, respectively, thermal conductivities of 7.19 and 7.15 units, yet their porosities are widely different, being 36.9 and 43.9 per cent. Samples C6622 and C6629 have conductivities of 5.99 and 7.15 units, with porosities of 44.9 and 43.9 per cent, respectively. C6622 has medium platy structure whereas C6629 has medium blocky. Samples C6617 and C6618 have conductivities 8.06 and 8.17 units, with porosities of 33.3 and 33.2 per cent. Both have medium blocky structures. These data given earlier (2)

for crushed and sieved samples, where structure has been destroyed and the soils reduced to packings of similar fragments, show, however, a close linear dependence on porosity. These examples show clearly that soil structure affects thermal transfer. The specific way in which it acts will be brought out later in the paper.

The faculty of the soil to transmit heat depends finally on the character of the solids that form the framework of the soil and of the liquids and gases that fill the voids throughout the framework. Consequently, if the porosity of the soil and the heat conductivities of the solid and fluid phases are known, the thermal conductivity of the soil can be calculated, provided the effect of structure can be evaluated.

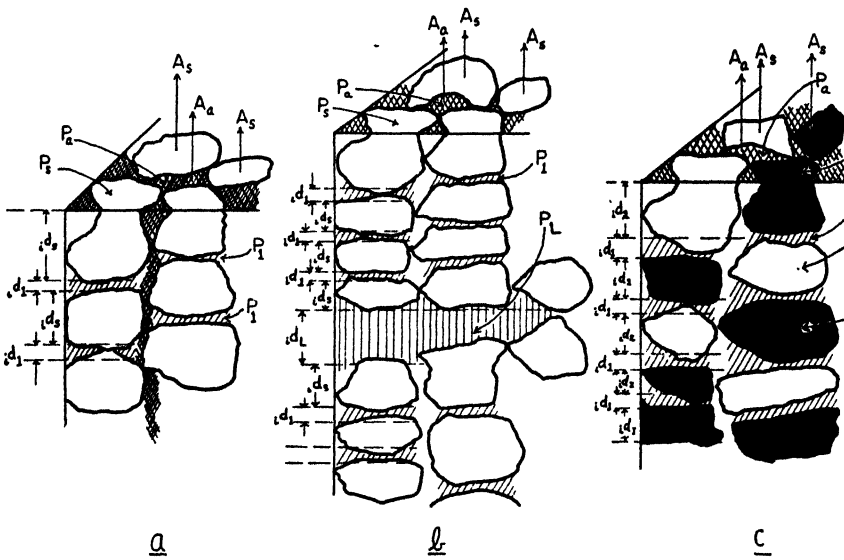

FIG. 4. SCHEMATIC REPRESENTATIONS OF CERTAIN SOILS: (a) STRUCTURELESS SINGLE-GRAINED SOIL; (b) STRUCTURED SOILS; (c) SOIL WITH SOLIDS OF TWO COMPONENTS

THERMAL TRANSFER IN STRUCTURELESS SOILS

For the starting point of a quantitative investigation let us take a thoroughly homogeneous loose structureless soil which naturally is characterized by a relatively uniform pattern of porosity throughout its extent. Such a soil is shown schematically in figure 4a. It is made up of single particles and voids filled with air.

Let us examine this mass of structureless, dry, single-grained soil bounded by two parallel planes, one at temperature t_1 and the other at t_2, such that $t_2 > t_1$. It is to be observed that in any sheet of material of conductivity k placed between two parallel planes and everywhere in close thermal contact with them, one at a temperature t_1 and the other at t_2, the temperature on any plane in the material, parallel to the boundary planes, is approximately constant when equilibrium prevails, and the flow of thermal energy is approximately normal to

these planes. In materials consisting of particles arranged in close contact such as a soil, there is little deviation of the level surfaces and lines of flow, from the simple system of orthogonal planes just postulated. Such as exists consists of slight oscillations about them.

The lines of flow approximately divide the soil under discussion into columns of air approximately paralleling columns of soil grains. The individual grains of the single soil column, in a dry soil, are, however, separated one from the other by voids filled with air, and the contacts are frequently point contacts. Since the thermal conductivity of air is much smaller than that of the mineral particles, the thermal resistance of the soil column and its included air is much greater than if the column were composed entirely of solid material. The pore space P_a thus functions, during heat transfer, in two ways. One part, designated by P_l introduces thermal resistance by series relation in the grain columns. The other $(P_a - P_l)$ conducts heat parallel to the soil columns. We shall compute the thermal resistance of the entire assemblage of columns and, thereby, the thermal conductivity of the soil. A schematic diagram for this purpose is presented in figure 4a, a three dimensional representation of a single-grain soil.

The thermal resistance R is defined by the equation $R = d/kA$ where k is the specific conductivity of the substance, A the area across which heat flows, and d the distance it flows (6, pp. 20–25). The thermal resistance R_a of the air column of length d_a and area A_a is

$$R_a = d_a/k_aA_a \quad \text{1}$$

The soil column of area A_a and of thermal resistance R_a consists of soil grains piled one on the other, each separated, as mentioned earlier, by an air gap of section A_l and effective thickness ${}_id_l$. A single grain of length ${}_id_s$ and its adjacent air gap are in series relationship (6, pp. 20–25) and have thermal resistance given by

$${}_cR_i = ({}_id_s/k_sA_s) + ({}_id_l/k_lA_l) \quad \text{2}$$

where k_s is the thermal conductivity of the soil grains and k_l that of the material in the gap (air in this case). The thermal resistance of the column will be the sum of many terms (one for each grain), each similar to those of equation 2, for series thermal resistances are additive.

The order of summation is here immaterial; k_s, A_s, k_l, and A_l are constant. If we set

$$\Sigma i\ {}_id_s = d_s \text{ and } \Sigma i\ {}_id_l = d_l$$

we obtain

$$R_c = d_s/k_sA_s + d_l/k_lA_l \quad \text{3}$$

as the thermal resistance of the column.

The total heat Q transmitted in unit time by the entire sample of sectional area A and thickness d is given by $Q = C\delta t$, where C is the thermal conductance (6, pp. 20–25) (the reciprocal of thermal resistance) effective under a tempera-

ture difference δt. For the mass of soil under discussion $\delta t = t_2 - t_1$. Since the air and soil columns are in parallel thermal relationship, the total conductance is obtained by adding the values obtained from equations 1 and 3; that is, $C = 1/R_a + 1/R_c$. Also, the specific thermal conductivity, k, of the sample, is defined by the equation $Q = kA\delta t/d$. Then, since $A_s = A_l$ and $d_a = d_s + d_l$, we have

$$Q = kA\delta t/d = \delta t[(k_a\Sigma A_a)/d + (\Sigma A_s)/\{(d_s/k_s) + (d_l/k_l)\}] \quad \ldots\ldots\ldots 4$$

where the summation extends over all the air and soil columns in the sample.

The value of k is found from equation 4 to be given by

$$k = k_a(\Sigma A_a)/A + [(\Sigma A_s)/A]/[(1/k_s)(d_s/d) + (1/k_l)(d_l/d)] \quad \ldots\ldots\ldots 5$$

From figure 4a it is evident that the quantities of the type $(\Sigma A_s/A)$, or (d_l/d) can be expressed in terms of volumes. Specifically, the volumes used are those of the soil, air, minerals, and water, or components of these, contained in a given volume of soil. The term "soil" as here used includes everything within the given volume—air, water, and soil framework. The volumes of each of the phases, or such parts of them as may be required, contained in unit volume, will be referred to as "soil partial volumes." Thus the partial volume of the voids is, when expressed in percentage, ordinarily called "porosity".

Accordingly, let $(P_a - P_l)$ be the partial volume of the soil air not effective in introducing thermal resistance in the grain columns; P_s that of the soil framework, i.e., the partial volume of the solids; P_l that of the material in the gaps between the grains, effective in introducing thermal resistance. Then, from figure 4a, it follows that $(d\Sigma A_a)/(dA) = P_a - P_l$. Hence,

$$(P_a - P_l) = (\Sigma A_a)/A \quad \ldots\ldots\ldots 6$$

Let us define P_c as the partial volume of a column of solid material and the matter within the gaps between its grains; then,

$$P_c = P_s + P_l \quad \ldots\ldots\ldots 7$$

also

$$P_c = (\Sigma A_s)/A \quad \ldots\ldots\ldots 8$$

Now,

$$(\Sigma A_s)d_l/Ad = P_l, \text{ and } d_l/d = P_l/P_c \quad \ldots\ldots\ldots 9$$

Also,

$$(\Sigma A_s)d_s/Ad = P_s, \text{ and } d_s/d = P_s/P_c \quad \ldots\ldots\ldots 10$$

With equations 6, 8, 9, and 10 it is possible to reduce equation 5 to

$$k = k_a(P_a - P_l) + P_c/\{(1/P_c)[(P_s/k_s) + (P_l/k_l)]\} \quad \ldots\ldots\ldots 11$$

The term k_aP_l is small compared to the sum of the terms remaining in the right member of equation 11, and will henceforth be neglected. A more general

form of equation 11 is given in the appendix and is applicable to cases where the solids consist of several components, for example, organic matter and minerals.

For the purpose of calculation it is convenient to transform equation 11. To this end, the partial volume, P_s, in the expression P_s/k_s, is replaced by $P_s = P_c - P_l$ (from equation 7). Since the soil is dry, $k_l = k_a$; finally we set

$$\alpha = P_l/P_s$$

and obtain

$$k = k_a P_a + P_s(1 + \alpha)/[(1/k_s) + \{(1/k_a) - (1/k_s)\}\{\alpha/(1 + \alpha)\}] \quad \ldots 12$$

which suffices for calculating the effective conductivity of a dry soil when the conductivities of air k_a, solid matter k_s, and the partial volumes P_a, P_s, and P_l are known.

As a simple example of the application of equation 12, let $P_a = 0$ and $P_l = 0$, then $P_s = 1$ and equation 12 reduces to $k = k_s$, the conductivity of the solid material, when it completely fills unit volume as a solid. The contact pore space is zero. In this connection it is to be observed that P_a includes all the contact pore space not effective in introducing thermal resistance in the grain columns in the direction of flow. The remainder, which is effective, is designated P_l. It is to be observed that $P_a + P_s + P_l = 1$, since the total volume of soil in unit cube is unity.

THERMAL TRANSFER IN STRUCTURED SOILS

Equation 12 is derived for a structureless single-grained soil. It is equally applicable to structured soils provided a proper value of P_l is chosen. Figure 4b shows a schematic representation of a structured soil. It will be noted that in a structured soil the voids are of two kinds; one comprising the pore space between individual soil particles (textural porosity), as in the structureless soil shown in figure 4a, and another comprising the pore space between structural aggregates (structural porosity). The structural porosity obviously introduces an additional thermal resistance superimposed on that of the structureless soil.

When structureless soils were considered it was concluded that the void space P_a introduces thermal resistance in a twofold way. A small part P_l of the contact pore space forming the gaps between adjacent grains introduces series thermal resistance in the direction of flow, whereas the larger remaining part $(P_a - P_l)$ introduces resistance parallel to the flow. From figure 4 it is evident that, for rectangular grains, the total contact pore space is roughly 3 P_l. In structured soils the structural pore space forms a network in which the structural aggregates are enmeshed. The aggregates function geometrically much as do the single grains of the structureless soil, as far as thermal resistance phenomena are concerned. There is a gap (fig. 4b) between adjacent aggregates, just as there is a gap between adjacent single grains, and this offers thermal resistance in the direction of flow by series relationship with the single aggregates. If P_L is the part of the structural pore space P_A, effective in introducing gap resistance, then $(P_A - P_L)$ introduces thermal resistance, in the aggregate assemblage, parallel to the direction of flow.

Simple considerations, and extension of equations 3, 7, 8, and 9, will show that P_l and P_L are additive, and that the net effect is to replace P_l of equation 12 by a new value, P_l', where $P_l' = P_l + P_L$. It is to be observed, for this purpose, that $A_l = A_L = A_s$. A_L is the cross-sectional area of that part of the structural pore space included within a given grain column of area A_s; d_l is to be replaced by $d'_l = d_l + d_L$. The value of P_l' is characteristic of the structure. We shall drop primes and simply understand that P_l is a term the value of which, in a given soil, depends upon the structure present. It is the component of the pore space which is effective in introducing thermal resistance during the passage of heat from grain to grain and from aggregate to aggregate. It consists of the pore space inserted between grain and aggregate contacts across which heat is transferred.

The remainder of the pore space $(P_A - P_L)$ consists of columns of air parallel to the columns of soil particles. The structural air columns are in parallel with the air columns defined for equation 1 for a structureless soil; that is, the columns within the aggregates. The area A_a is the sum of the areas of the textural and structural air columns as shown in figure 4b, and d_a is the same for each. Hence, in equation 11, the term $k_a(P_a - P_l)$ requires no modification, provided P_a be taken as the total pore space; that is, the sum of the textural and structural porosities. Equation 12 is then applicable to structured soils, if P_a is taken as the total pore space and P_l is chosen for the particular structure present. The term k_aP_l can be neglected, as in equation 12, since it is small, even in structured soils, compared to the remaining terms of the right member of this equation.

Effect of ordinary structural types on thermal transfer

The relative orders of the values of the structural partial volume P_l can be established for ordinary structures from simple considerations of the shape of the air gaps offering thermal resistance between structural units, and their frequency of occurrence, both of which depend upon the shape and size of the structural aggregates. The influence of structural pore space, that is the network of cavities in which structural aggregates are enmeshed, upon the thermal conductivity of a soil, can be more clearly explained by such considerations.

The air gaps between granular aggregates are relatively large and generally are bounded by two oppositely convex surfaces, as shown in figure 5d. Because of the rather small size of these aggregates the frequency of air gaps is large. Hence the value of P_l should be greater than for other types of soil structure.

Platy structure (fig. 5a) is characterized by narrower gaps, lying close to one another because of a generally small thickness of the platy aggregates. Hence the gaps are frequent, as in granular structure, but because of their narrowness they offer less thermal resistance, and the value of P_l is smaller than that for granular structure. Consequently platy structure offers less thermal resistance than granular structure.

The air gaps between the units of blocky structure (fig. 5b) are usually small,

but the blocks themselves are relatively large. Hence, the frequency of gaps is small, the value of P_l is still smaller, and consequently the thermal resistance of the soil having blocky structure should be less than that of the soil having either granular or platy structure. Obviously, the frequency of gaps is larger

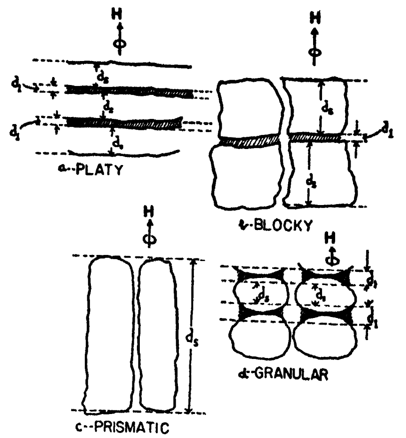

FIG. 5. COMPARISON OF SHAPES OF AIR GAPS IN SOME COMMON STRUCTURES: (a) PLATY, (b) BLOCKY, (c) PRISMATIC, (d) GRANULAR. THE ARROW, H, SHOWS THE DIRECTION OF HEAT TRANSMISSION

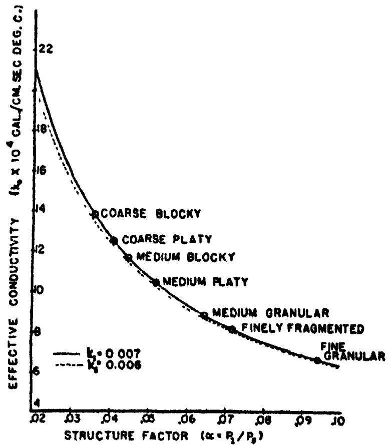

FIG. 6. RELATION BETWEEN STRUCTURE AND EFFECTIVE CONDUCTIVITY

Reduction of the natural structure to the finely fragmented state is accompanied by a large alteration of the structure factor α and hence of the effective conductivity of the soil

and P_l is greater in the soils having blocky structures of finer classes than in those characterized by a coarse structure.

Prismatic (fig. 5c) structure will offer still less thermal resistance and a smaller value of P_l. The massive structureless soil offers least thermal resistance and is characterized by close thermal contacts of individual grains. The values of

P_l and its associated thermal resistance for such a soil should be exceedingly small. P_A, the structural pore space, vanishes for the massive condition.

Thus it appears that the size of the air gaps and their frequency of occurrence, which are determined by the size of the aggregates, determine the thermal resistance in a given natural soil. These quantities, when known, should be sufficient to determine P_l.

Approximate calculation and values of the thermal structure factor

Methods to obtain the values of P_l, required for even ordinary structures, do not appear at present to be obtainable from theoretical considerations. Values of $\alpha = P_l/P_s$ may, however, be calculated from the observed data, and some conclusions reached on its behavior.

For this purpose, we observe that equation 12 has the simple form

$$k = k_a P_a + k_0 P_s \quad \ldots\ldots 13$$

where

$$k_0 = (1 + \alpha)/[(1/k_s) + \{(1/k_a) - (1/k_s)\}\{\alpha/(1 + \alpha)\}] \quad \ldots\ldots 14$$

We shall call k_0 the effective conductivity of the soil.

Equation 14 may be solved for α, and leads to the quadratic equation

$$(1/k_0)\alpha^2 + \{(2/k_0) - (1/k_a)\}\alpha - \{(1/k_s) - (1/k_0)\} = 0 \quad \ldots\ldots 15$$

Equation 15, when solved, yields the value

$$\alpha = \{(1/2)(k_0/k_a) - 1\} + \{(1/4)(k_0/k_a)^2 - [(k_0/k_a) - (k_0/k_s)]\}^{\frac{1}{2}} \quad \ldots 16$$

To obtain values of k_0 from the experimental data for use in calculating α by equation 16, the following equation, obtained by solving equation 13 for k_0 may be used:

$$k_0 = (k - k_a P_a)/P_s \quad \ldots\ldots 17$$

In addition to the values of k_0, calculated from the data by use of equation 17, values of k_s and k_a must be known when finding α from equation 16. Now, k_a has the value 0.000057 cal./cm. sec. deg. C, since the material in the soil is air. For the Miami soils the parent material has a conductivity $k_s = 0.0070$. The latter value is estimated from the data of Birch and Clarke (2) on the assumption that the parent material, glacial till, consists of limestone, granite, and gneiss and their weathered products. The assumption involved is that the conductivity k_s of the mineral component does not differ greatly in the weathered and unweathered condition. [Compare (2, table 6).] The Chester is derived from gneiss, with a value of $k_s = 0.0060$ cal./cm. sec. deg. C.

Values of k_0 have been calculated by equation 17 from the data of table 1; with these values, the corresponding structure factors, $\alpha = P_l/P_s$, were calculated for dry soils by equation 16. Table 2 summarizes the results. From these data the following values of the structure factor, for use in equation 12, are indicated.

$$\begin{aligned} P_l/P_s &= 0.065 \text{ for medium granular structure} \\ P_l/P_s &= 0.052 \text{ for medium platy structure} \\ P_l/P_s &= 0.041 \text{ for coarse platy structure} \\ P_l/P_s &= 0.045 \text{ for medium blocky structure} \\ P_l/P_s &= 0.036 \text{ for coarse blocky structure} \end{aligned} \tag{18}$$

These values are for well-developed structures. Moderate development will probably result in a slight lowering, and poor development will produce a greater shift toward values characteristic of the massive condition. Poor development of structure probably accounts for the lower structure factors given in table 2

TABLE 2
Summary of thermal structure factors

SAMPLE NUMBER	k_0*	P_l/P_s	STRUCTURE	
			Type and class	Estimated dimensions
				cm.
C6615	6 61	.094	Fine granular	0.1 to 0.3
C6616	10.61	.051	Medium platy	0.2 to 0.4
C6617	11 79	.045	Medium blocky	0.8 to 2
C6618	11 94	.044	Medium blocky	1 to 2.5
C6619	12.64	.039	Coarse blocky	1 to 3
C6620	11 06	.046	Medium blocky	. ..
C6621	8 87	.069	Medium granular	.
C6622	10.43	053	Medium platy	. ..
C6623	12 48	041	Coarse platy	0 16
C6624	11.48	.045	Medium blocky	0.6 to 1.9
C6625	11 10	.047	Medium blocky	1.3 to 1 9
C6626	13.50	.036	Coarse blocky	.
C6627	9.44	059	Medium blocky	
C6628	9 90	.060	Medium granular	0 5 to 0.1
C6629	12.30	.041	Medium blocky	1 to 2
C6630	9 46	.054	Fine platy	0 1 to 0.2

* 10^{-4} cal./cm. sec. deg. C.

for the Chester soil. The values given in equation 18 are tentative, since they are based on data limited to the three profiles given in table 2. Further data on other profiles may show departures from the values given because of differences in well-developed structures.

Empirical calculation of coefficients of thermal conduction

Equations 13 and 14 are sufficient to calculate the thermal conductivity of a soil from field data, provided the structure factor $\alpha = P_l/P_s$ is known. It appears that such must be found from thermal measurement, for the present, and until more specific morphological investigations, experimental and theoretical, lead to an independent approach.

Since the data of table 3 indicate that characteristic values exist for each type of structure, we shall use the mean values given by equation 18, and compute the thermal conductivities of the soils listed in table 1. The value $\alpha = 0.095$ is probably required for very fine granular structure. The value $P_l/P_s = 0.036$ is probably equally applicable to coarse or poorly developed blocky structure. The value for the massive condition is possibly as low as 0.030; and that for the single grain condition, in excess of 0.090.

Table 3 compares observed and empirically computed values of thermal conductivity: column 2 lists observed values; column 3, values computed from equations 13 and 14 with structure values given by equation 18; column 4, the

TABLE 3

Summary of observed and calculated (empirical) values of thermal conductivity

SAMPLE NUMBER	THERMAL CONDUCTIVITY* (OBSERVED)	THERMAL CONDUCTIVITY* (CALCULATED)	k_0* CALCULATED FROM EQ 17	k_s†	P_l/P_s
C6615	3.3	3.3	6.66	.0070	.094
C6616	7.4	7.3	10.45	.0070	.052
C6617	8.1	8.1	11.80	.0070	.045
C6618	8.2	8.1	11.80	.0070	.045
C6619	8.4	9.2	13.80	.0070	.036
C6620	7.2	7.7	11.80	.0070	.045
C6621	4.2	4.1	8.82	.0070	.065
C6622	6.0	6.0	10.45	.0070	.052
C6623	7.8	7 7	12.30	.0070	.041
C6624	7.5	7.7	11.80	.0070	.045
C6625	6.9	7.3	11.80	.0070	045
C6626	9.2	9.4	13.80	.0070	.036
C6627	6.2	7.7	11.80	.0070	.045
C6628	4.9	4.3	8.66	.0060	.065
C6629	7.2	6.7	11.30	.0060	.045
C6630	5.2	5.7	10.25	.0060	.052

* 10^{-4} cal./cm. sec. deg. C.

† cal./cm. sec. deg. C.

values of k_0 used in equation 16 to compute the values of column 3; columns 5 and 6 list, respectively, the values of k_s and P_l/P_s used in equation 17 to compute the values of k_0 shown in column 4. The value of P_l/P_s required for medium platy structure has been used for the Chester C (sample C6630). The latter has a poorly developed fine platy structure, probably an original characteristic of the particular parent material, inherited by the soil, and, perhaps, unmodified by the development of the soil profile. Closer agreement might be attained between observed and calculated values of the thermal conductivities, by more careful determination of the structure factors; but this would require additional morphological studies and data.

Discussion

It should be borne in mind that thermal resistance is introduced by air gaps in the soil, and this whether in a texture packing or structure, or related phenomena such as shrinkage fissures. Structure is the usual agent producing such gaps. If, for example, poorly developed blocky structure exists, its effect will perhaps be close to coarse blocky, characterized by few gaps, or even the massive condition. The gaps in this case would not be completely developed. The thermal resistance when dry would not be so great as in a well-developed structure because of the deficiency of gaps which introduce thermal resistance in series with the columns of structural units. Shrinkage fissures introduce thermal resistance in series or parallel or both, much as do structural gaps. The resistance developed depends, as with structured soils, on the distribution and width of the gaps. Variations in texture, doubtless, are accompanied by changes in the shape and frequency of the small air gaps between single particles of a structured unit. The porosity and therefore the thermal conductivity undergo, in similar structure units, corresponding variations as texture changes.

Attention, in this connection, is directed to samples C6620 and C6627. These samples represent vertical sections through the B horizons which are characterized by blocky structure. The thermal conductivity of these samples is somewhat less than that of the horizontal samples cut from the same soil horizons. Perhaps this demonstrates the effect of the width of the air gaps on thermal resistance. It is a rather common characteristic of blocky structure that the cracks running vertically are markedly wider than those which run horizontally, since the latter are continually under load. The structure factors for the vertical sections are, therefore, closer to those for platy structure, as given by equation 18, since this equation rests on data for vertical transmission through ordinary horizons. Anisotropic conduction in a dry, structured soil is indicated by these data. Since P_l/P_s includes not only a component of the pore space between structural units, but also a component of the contact pore space between grains, the increased thermal resistance of vertical sections may indicate anisotropy in the contact pore space also. The latter is improbable but can only be ruled out by experimental work, specific for the purpose.

FINELY FRAGMENTED DRY SOILS

The physical behavior and properties of soils reduced mechanically to a fine state of division have been extensively investigated. Many of the conclusions reached have been assumed to apply equally to natural soils, that is, to soils in which the configuration and properties existing in the natural landscape are unaltered. As a matter of fact, some properties are independent of the state of physical division, but there is serious doubt as to whether this is generally so. Data are presented in this section to show that thermal transfer is greatly affected by the state of division of the soil. Specifically, a comparison is made between results obtained from natural soils, and those obtained on the identical soils reduced to a finely fragmented state.

After measurement, the monolith samples were reduced to a state of fine frag-

mentation by the usual laboratory procedure. The samples were lightly rolled until they had been broken down sufficiently to pass a 2-mm. sieve; all stony and other material which could not easily be broken down was rejected. A given soil, upon completion of the treatment, has been reduced to an assemblage of microfragments.

The reduced soils were then packed, for thermal measurement, in hard rubber frames closed by face plates of hard rubber. The method of packing, as well as the procedure used for the thermal measurements, are described in a preceding publication (10). The porosity was determined from the weight of the soil, the known volume of the frame, and the density of the soil solids. The moisture content was determined by oven-drying small samples obtained just before packing. To study the thermal transfer of moisture, samples of soil were taken from both the warm and the cold sides of the samples just after

TABLE 4

*Observed thermal conductivities and related data of finely fragmented soils**

SAMPLE NUMBER	THERMAL CONDUCTIVITY†	POROSITY	VOLUME WEIGHT	SAMPLE NUMBER	THERMAL CONDUCTIVITY†	POROSITY	VOLUME WEIGHT
		per cent	*gm./cc.*			*per cent*	*gm./cc.*
C6615	3.46	61.4	1 00	C6623	4.80	51.5	1.30
C6616	4.95	46.5	1.45	C6624	4.06	54 4	1.24
C6617	3.68	59.0	1.12	C6625	4.43	56.6	1.19
C6618	4.21	50.0	1 37	C6626	5.26	44.8	1.53
C6619	4 94	50.2	1 37	C6627	4.39	55 0	1 23
C6620	4.00	55 5	1.22				
				C6628	3.80	59.6	1.09
C6621	3.75	57.2	1.11	C6629	4.41	54.7	1.25
C6622	4.37	53.6	1.24	C6630	4.57	56.7	1.23

* Compare with data for corresponding samples of natural structure (table 1).
† 10^{-4} cal./cm. sec. deg. C.

thermal measurement. The observed moisture shift is too small to affect the results reported in this paper.

Table 4 summarizes thermal data on the finely fragmented samples. It will be observed that where the soil has a granular structure such as that shown by samples C6615, C6621, and C6628 (see table 2), the thermal conductivities are not very different from those of the natural structure (see table 1). For example, number C6615, the A_1 horizon of Miami silty clay loam, has a very fine granular structure with thermal conductivity 3.27 units; when it is reduced to the finely fragmented condition the thermal conductivity is 3.46 units. The porosities and volume weights, in the two states, are not widely different. When, however, the structure is blocky, the thermal conductivity is almost twice that observed in the finely fragmented state. Sample C6618 serves as an illustration of this. The thermal conductivity is 8.17 units when in medium blocky aggregation and only 4.21 units in the finely fragmented state. Corresponding changes are shown in the porosities and volume-weights of the two states.

After fragmentation, the thermal conductivities of all the horizons given have values which do not differ greatly. Small variations are to be expected because the structure factor (P_l/P_s) for the finely fragmented state should be approximately the same for all soils, since the aggregates are approximately of the same size and shape. Such differences in conductivity as arise should occur primarily from alterations in porosity and, to a slight degree, from differences in mineral composition. If the thermal conductivities of fragmented soils be plotted as a function of their porosities, the resulting curves will be linear and the data will fit closely. The value of the effective conductivity k_0 in the fundamental equation $k = k_aP_a + k_0P_s$ depends on the structure factor $\alpha = P_l/P_s$ and this varies but little for most finely fragmented soils. With natural soils, however, the data will only roughly approximate a straight line, because of the larger variation of k_0 caused by the wider range of values of the structure factor α.

TABLE 5

*Thermal structure factors of soils in the finely fragmented state**

SAMPLE NUMBER	STRUCTURE FACTOR, P_l/P_s	EFFECTIVE CONDUCTIVITY, k_0†	SAMPLE NUMBER	STRUCTURE FACTOR, P_l/P_s	EFFECTIVE CONDUCTIVITY, k_0†
C6615	.075	8 06	C6623	.061	9.30
C6616	.066	8 78	C6624	.071	8 24
C6617	.072	8.16	C6625	.058	9 57
C6618	.075	7 86	C6626	.063	9.06
C6619	.060	9.34	C6627	.060	9.37
C6620	.071	8 28			
			C6628	.065	8.59
C6621	.074	8 00	C6629	.063	9.06
C6622	.066	8 79	C6630	.056	9.82

* Compare with data for corresponding samples of natural structure (table 2).
† 10^{-4} cal./cm. sec. deg. C.

A summary of values of structure factors and effective conductivities is recorded in tables 5 and 6. The structure factors, $\alpha = P_l/P_s$, are calculated from equation 18. The effective conductivities were determined from the experimental data by use of equation 17.

Table 5 records data for Miami silty clay loam, Miami silt loam, and Chester loam. Comparison with table 2 shows the effect on the structure factor of reducing a natural soil to a state of fine fragmentation. The finely reduced soils have structure factors ranging from 0.056 to 0.075. These values have the order of magnitude of naturally granular soils, which run from 0.060 to 0.094. The medium blocky soils have structure factors between 0.041 and 0.047, but when these soils are finely fragmented the values increase, ranging from 0.056 to 0.075. Similar behavior is shown by the coarse blocky soils. Apparently little difference appears in the Chester C (sample C6630) in either the natural or the reduced state. By comparison with table 2, it is seen that the effective conductivities of the natural state, which range from 6.61×10^{-4} to 13.5×10^{-4},

are brought to the range, 7.9×10^{-4} to 9.8×10^{-4}, by the process of fine mechanical fragmentation. Destruction of the structural pore space of a natural soil and replacement by a new secondary pore space (that between the fragments of the mechanically fragmented soil) is seen, therefore, to result in an increase in thermal resistance and therefore in a lowering of the power of a soil

TABLE 6

Summary of thermal structure factors for oven-dried finely fragmented soils

SAMPLE NUMBER	SOIL	HORIZON	EFFECTIVE CONDUCTIVITY*	STRUCTURE FACTOR, P_l/P_s	SAMPLE NUMBER	SOIL	HORIZON	EFFECTIVE CONDUCTIVITY*	STRUCTURE FACTOR, P_l/P_s
C3181	Hermon	A_1	6.66	.094	8736	Marshall silt	0–13″	8.74	.067
C3182	sandy	A_2	7.36	.082	8737	loam	13–24″	8.84	.065
C3183	loam	B_1	7.32	.083	8739		45–71″	8.52	.068
C3184		B_2	8.22	.071					
C3185		B_3	7.45	.081	C2929	Barnes loam	A	7.34	.083
C3186		C	8.06	.073	C2930		B_1	8.32	.071
					C2931		B_2	8.85	.065
C3187	Kalkaska	A_1	6.30	.101	C2932		C	8.28	.071
C3188	loamy	A_2	8.62	.067					
C3189	sand	B_1	7.90	.080	161	Ruston	A	8.30	.070
C3190		B_2	7.57	.074	162	loamy sand	B	7.66	.073
C3191		C	7.66	.073	163		C	8.42	.069
C3174	Russell silt	A_1	7.50	.080	C3866	Cecil sandy	A	7.88	.075
C3175	loam	A_2	7.16	.085	C3867	clay loam	B_1	9.26	.061
C3176		A_3	7.04	.087	C3868		B_2	8.72	.061
C3177		B_1	7.64	.078					
C3178		B_2	7.96	.074	C3871	Kirvin fine	0–10″	8.56	.068
C3179		B_3	7.94	.074	C3872	sandy loam	10–24″	8.27	.071
C3180		C	7.34	.083	C3873		24–60″	8.82	.065
C1671	Chester	A	7.38	.085	C3906	Nacogdoches	0–10″	8.20	.072
C1672	loam	B	9.15	.062	C3908	fine sandy	10–44″	8.44	.069
C1673		C	8.46	.064	C3909	loam	44–70″	8.12	.073
C2916	Carrington	A_1	7.84	.076	9804	Columbiana	A_1	8.48	.069
C2917	loam	A_2	7.56	.075	9805	clay	A_2	8.85	.065
C2918		B_1	8.91	.064	9806		A_3	8.52	.068
C2919		B_2	8.90	.064	9807		B_1	7.64	.078
C2920		B_3	8.22	.071	9808		B_2	7.81	.076
C2921		C	7.29	.083	9809		C	7.96	.074

* 10^{-4} cal./cm. sec. deg. C.

to conduct heat. By such a process the relatively high conductivities of coarse blocky structure, for example, are reduced to the lower values which characterize naturally granular soils.

Table 6 tabulates values of the structure factor and the effective conductivity of a number of finely fragmented soils, all oven-dried. Computations are from

TABLE 7

Comparison of observed and calculated (empirical) values of thermal conductivities of air-dried soils

$k_0 = 8.10 \times 10^{-4}$ cal./cm. sec. deg. C.; $\alpha = 0.072$

SAMPLE NUMBER	THERMAL CONDUCTIVITY*		SAMPLE NUMBER	THERMAL CONDUCTIVITY*	
	Observed	Calculated		Observed	Calculated
C6615	3.3	3.5	C6623	4.4	4.2
C6616	4.8	4.6	C6624	4.1	4.0
C6617	3.8	3.7	C6625	4.0	3.8
C6618	4.5	4.3	C6626	4.9	4.7
C6619	4.5	4.3	C6627	4.1	4.0
C6620	4.1	3.9	C6628	3.7	3.6
C6621	3.9	3.8	C6629	4.1	4.0
C6622	4.2	4.1	C6630	4.0	3.8

* 10^{-4} cal./cm. sec. deg. C.

TABLE 8

Comparison of observed and calculated (empirical) values of thermal conductivities of oven-dried soils

$k_0 = 8.10 \times 10^{-4}$ cal./cm. sec. deg. C.; $\alpha = 0.072$

SAMPLE NUMBER	THERMAL CONDUCTIVITY*		SAMPLE NUMBER	THERMAL CONDUCTIVITY*	
	Observed	Calculated		Observed	Calculated
C3181	1.6	1.4	8736	3.9	4.1
C3182	5.3	4.8	8737	3.8	4.1
C3183	3.9	3.6	8738		
C3184	4.8	4.9	8739	4.4	4.6
C3185	5.1	4.7	C2929	3.8	3.4
C3186.	6.0	5.9	C2930	3.7	3.8
C3187	1.9	1.6	C2931	3.8	4.1
C3188	4.8	5.1	C2932	4.1	4.2
C3189	4.4	4.3	161	4.9	5.0
C3190	4.7	4.4	162	4.1	3.9
C3191	4.9	4.6	163	4.3	4.4
C3173			C3866	4.2	4.1
C3174	3.4	3.2	C3867	4.2	3.9
C3175	4.3	3.8	C3868	3.4	3.7
C3176	4.4	3.9	C3871	4.2	4.4
C3177	4.2	3.9	C3872	4.0	4.1
C3178	4.3	4.3	C3873	3.8	4.1
C3179	4.3	4.2	C3907	4.0	4.0
C3180	4.6	4.2	C3908	3.4	3.5
C1671	3.7	3.3	C3909	3.4	3.4
C1672	3.5	3.9	9804	3.5	3.6
C1673	3.8	3.9	9805	3.2	3.5
C2916	3.6	3.5	9806	3.2	3.3
C2917	3.9	3.6	9807	3.1	2.9
C2918	4.1	4.4	9808	3.2	3.1
C2919	4.0	4.4	9809	3.3	3.2
C2920	3.8	3.9			
C2921	4.4	4.8			

* 10^{-4} cal./cm. sec. deg. C.

measurements reported in another paper (9). Measurements, in the natural state, were not made on the soils given in this table, so that no comparison can be made. It will be observed, however, that the effective conductivities and structure factors have about the same range as those of the finely reduced state listed in table 5.

Figure 6 is a complete graph of effective conductivity, k_0, represented as a function of the structure factor α as computed from equation 16. The values for natural structures with large aggregates such as blocky are associated with large effective conductivities, whereas the value for the finely fragmented state is at the low end of the curve and lies between those of the natural structures, medium and very fine granular. Each of the values characterizing the several morphological states of soils, as given by equation 18, is indicated by a circle on the curve.

A knowledge of the structure factor enables us to calculate the thermal conductivity k of a dry soil (equations 13 and 14). Again as with structured soils, an empirical method is used. The average value of α from the data of table 6, for oven-dried soils, is $\alpha = 0.072$. The effective conductivity computed from equation 14 is 8.10×10^{-4} cal./cm. sec. deg. C. This is an average of the values of k_0 for values of $k_s = 0.006$ and $k_s = 0.007$ cal./cm. sec. deg. C., since the separate values of k_0 do not materially differ (as shown in figure 6).

Tables 7 and 8 summarize values of observed thermal conductivity and values calculated from equation 3 with $k_0 = 8.10 \times 10^{-4}$ cal./cm. sec. deg. C., the value found by the method given in the last paragraph. Table 7 includes Miami silty clay loam, Miami silt loam, and Chester loam. Table 8 represents the results of the calculation for the soils listed in table 6. The agreement appears sufficient to warrant the use of the value $\alpha = 0.072$ in equations 13 and 14 for calculating the thermal conductivity of finely fragmented soils.

THERMAL CONDUCTIVITY OF PEAT SOLIDS

Values do not exist in the literature for the thermal conductivity of peat solids. Equation 16 may be solved for k_s, as follows:

$$k_s = 1/[\{(1 + \alpha)^2/k_0\} - \{\alpha/k_a\}] \qquad \text{19}$$

With the data reported in an earlier paper (9, table 7), the effective conductivity k_0 of sedge peat packed to a volume-weight of 0.354 gm./cc. was found by equation 17 to be 4.90×10^{-4} cal./cm. sec. deg. C.; that of reed cultivated peat was found similarly to be 4.75×10^{-4} cal./cm. sec. deg. C. when it was packed to a volume-weight of 0.430 gm./cc. The values of k_s (the conductivity of the peat solids) computed from equation 19 with these values of k_0 and a value of $\alpha =$ 0.065, are found to be respectively 0.00086 cal./cm. sec. deg. C. for sedge peat, and 0.00080 cal./cm. sec. deg. C. for reed peat. The value $\alpha = 0.065$, that of medium granular structure, was used rather than $\alpha = 0.072$ for a finely fragmented soil, since it was felt that sieving does not materially change the state of division of the peat solids.

Moss peat packed to a volume-weight of 0.070 has an effective conductivity

$k_0 = 0.0015$ cal./cm. sec. deg. C. A structure factor greater than $\alpha = 0.030$ does not appear consistent with the data. The fibers are close-packed, much like an ideal platy soil structure. Further, the fibers are single units and are not composed of piled particles, as is the case in an ordinary soil granule. Hence the thermal resistance in the direction of transmission arises chiefly from air between the packed fibers and very little from air within single fibers. A value of $\alpha = 0.030$ gives a value for the conductivity, k_s, of the moss peat solids, of 0.00574 cal./cm. sec. deg. C.; $\alpha = 0.020$ gives $k_s = 0.00239$ units; $\alpha = 0$ gives $k_s = 0.00151$ units. The value $k_s = 0.00239$ units is probably closer to the real value than the others. Cellulose packed to a volume-weight of 1.4 gm./cc. has a conductivity $k = 0.000582$ cal./cm. sec. deg. C. (5, p. 314). Its effective conductivity is $k = 0.00163$ cal./cm. sec. deg. C.

The value $\alpha = 0.020$, used previously for moss peat, places the conductivity of the cellulose solids approximately equivalent to that of moss peat. The values given for the thermal conductivities of peat solids are not definite, because of the uncertainty in the structure factors α involved. Further investigation is needed before any great reliability can be attached to them.

SUMMARY

Methods for cutting large monolith samples are given. Measurements of thermal conductivity on monolith samples cut by these methods are reported for Miami silt loam, Miami silty clay loam, and Chester loam. They show wide variation depending on the structure present. Data are also given for these samples when reduced to the finely fragmented state. The thermal conductivities, except for granular structures, are considerably decreased when the soils are reduced to this state.

Approximate expressions for the calculation of the thermal conductivity of a dry soil are developed. These require for their use in natural soils specific data regarding the porosity (determined usually from field volume-weights and textural density), the soil structure, and the respective thermal conductivities of the soil solids and fluids.

The influence of structure on thermal resistance is discussed and an index α (thermal structure factor) established for measuring its effect. It depends on the type, class, and grade of structure. It appears from theoretical consideration, that the thermal resistance of the soil depends in a twofold way on the porosity: first, on the part of the pore space in parallel with the pilings of soil grains in the direction of heat transmission; and, second, on the part of the pore space inserted between adjacent grains of these pilings. The component of the latter between structure units is principally effective in producing the large variations observed in soils of natural structure.

Thermal conductivities of dry natural soils are generally altered whenever these soils are reduced to a state of fine fragmentation. The process of comminution destroys the structural pore space and substitutes a new secondary pore space, which is that between the fragments resulting from the reduction. The textural pore space of the fragments is not materially altered. Granular struc-

tured horizons have about the same conductivity in both the natural and the reduced states. Mechanical reduction as usually done in the laboratory has little effect on ordinary granular structures. The thermal conductivity of most other structure patterns differs greatly from that observed in the finely fragmented condition, and in some cases it may be twice that observed in the reduced state.

Thermal resistance is a property dependent on the architecture of the pore space and, in particular, on the component of the pore space included within the thermal paths through the soil solids. It appears to depend both upon the textural and the secondary pore spaces. So far as the secondary pore space is concerned, the dependence is on the structural, if the soil is natural and structured; and, if it is in the mechanically fragmented state, the dependence is on that between the fragments. The component of the secondary pore space included within the thermal paths through the soil solids differs significantly in each type of secondary pore space; hence, the thermal resistance and, therefore, the conductivity are generally different in each of these states.

APPENDIX

When the solid part of the soil consists of n components having volumes $P_1, P_2, P_3 \cdots P_n$ and thermal conductivities $k_1, k_2, k_3 \cdots k_n$ respectively, the general expression for the thermal conductivity of the multicomponent system so formed may be derived by an extension of the procedure used to derive equation 12.

From figure 4c, the thermal resistance of a single column of grains is given by $R_c = (1/A_s)\{(1/k_1)\Sigma d_1 + (1/k_2)\Sigma d_2 + \cdots (1/k_l)\Sigma d_l\}$ Since the columns are in parallel with the air columns the total heat transmitted by the soil in unit time is $\Sigma q = \delta t(C_s + C_a)$ where C_s is the total conductance of the soil columns, and C_a, that of the air columns.

Since $(kA\ \delta t)/d = \Sigma q$
we find

$$k = [(\Sigma A/A_s)/\{[1/k_1]\,[(\Sigma d_1)/d] + [1/k_2]\,[(\Sigma d_2)/d] + \cdots$$
$$\cdots [1/k_n]\,[(\Sigma d_n)/d] + [1/k_l]\,[(\Sigma d_l)/d]\}] + (k_a)\,[(\Sigma A_a)/A]$$

The following auxiliary relations exist and may be verified by referring to figure 4c:

$$P_c = (\Sigma A_s)/A$$
$$P_1 = (A_s)\ (\Sigma d_1)/(Ad);\ (\Sigma d_1)/d = P_1/P_c$$
$$P_2 = (A_s)\ (\Sigma d_2)/(Ad);\ (\Sigma d_2)/d = P_2/P_c$$
$$P_n = (A_s)\ (\Sigma d_n)/(Ad);\ (\Sigma d_n)/d = P_n/P_c$$

Hence

$$k = [P_c/\{(1/k_1)(P_1/P_c) + (1/k_2)(P_2/P_c) + (1/k_n)(P_n/P_c) + (1/k_l)(P_l/P_c)\}] + k_aP_a$$

Since $P_c = P_s + P_l$

also $P_s = P_1 + P_2 \cdots P_n$

where P_s is the total volume of solids,
then

$$k = [(1 + \alpha)/\{[(1/k_1)(P_1/P_s) + (1/k_2)(P_2/P_s) + \cdots (1/k_n)(P_n/P_s) + (1/k_l)(P_l/P_s)][1/(1 + \alpha)]\}]P_s + k_aP_a \qquad 1$$

where $\alpha = (P_l/P_s)$.

As a particular example, let the solid matter consist of two components, one a mineral and the other organic matter, then if P_m and k_m denote respectively the partial volumes

and conductivity of the mineral component, and P_0 and k_0 the corresponding quantities for the organic matter, equation 1 reduces to

$$k = [(1 + \alpha)/\{[(1/k_m)(P_m/P_s) + (1/k_0)(P_0/P_s) + (1/k_l)(P_l/P_s)][1/(1 + \alpha)]\}]P_s + k_a P_a. \quad 2$$

Further development of the theory given above is possible by considering that the soil columns oscillate slightly along the long axis instead of following it as in figure 4. Rough approximation will lead to an equation in which $(k/\cos^2\theta)$ equals the right member of equation 1; θ is the average deviation of a single grain from the long axis of the column. The factor $\cos^2\theta$ will be close to unity, and equation 1 will not be materially altered

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INFLUENCE OF LOW RECESSIONAL MORAINES ON SOIL TYPE PATTERN OF THE MANKATO DRIFT PLAIN IN IOWA[1]

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The pattern of Clarion and Webster soils in north-central Iowa has been thought to be a haphazard one due to random distribution of ridges and depressions over the surface of the Mankato (Late Wisconsin) ground moraine (7). Recent study of aerial mosaics prepared for county areas by the Agricultural Adjustment Administration, however, has disclosed the existence of a belted or banded arrangement of swells and swales over much of the area (2). This arrangement, not readily apparent from the ground, is interpreted as a sequence of annual recessional moraines, low ridges that are separated by shallow swales. These low moraines are important in determining the present pattern of soil types. Recognition of the relation between the pattern of moraines and that of soil types should be helpful in the classification and detailed mapping of soils in the area of the Mankato lobe[3] and in comparable regions elsewhere. A discussion of the nature and arrangement of the low moraines and their influence on soil type pattern is offered in this paper.

DESCRIPTION OF THE REGION IN IOWA

The Mankato lobe

An area (3) of approximately 10,000 square miles in north-central Iowa, corresponding to the region of the Clarion-Webster soil association, is underlain by drift deposited during the Mankato substage of the Wisconsin glaciation. This drift sheet, in the form of the lobe shown in figure 1, is approximately 130 miles wide along the Iowa-Minnesota border and extends southward into Iowa for a similar distance.

The area is a comparatively level plain in the initial stage of the erosion cycle. The relief of individual square miles in the unmodified parts of the plain may range up to 10 or 15 feet but in many places is less than 5 feet. In the southern part of the drift plain, major streams have cut narrow valleys to depths as great as 200 feet below the general level. These narrow valleys are bordered by dissected and hilly belts ranging up to a few miles in width. Other belts of rolling to hilly lands rising above the general level occur at the margins of the lobe as terminal moraines or within the lobe as areas of larger recessional moraine or of drift-mantled pre-Mankato topography. Most of the area of 10,000 square miles,

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[3] The Mankato lobe is synonymous with the Des Moines lobe of earlier literature.

however, has a gentle swell and swale topography. Drainage channels are few and poorly developed, and runoff is frequently restricted. Variations in natural drainage conditions are reflected in the pattern of soil types that occupy the region.

Soils of north-central Iowa

Two series, the Clarion, representing the zonal group of prairie soils, and the Webster, representing the intrazonal group of Wiesenboden, predominate over the area. Other soil series such as the Dickinson, Pierce, Sioux, Lamoure, and

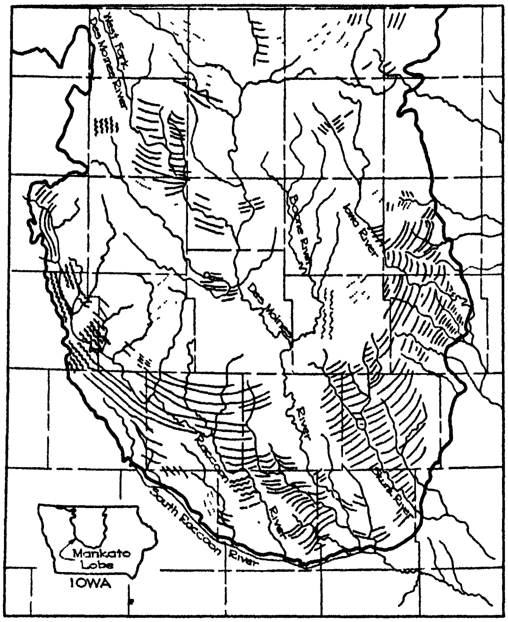

FIG. 1. SKETCH MAP SHOWING APPROXIMATE EXTENT AND GENERAL PATTERN OF ANNUAL RECESSIONAL MORAINES ON THE MANKATO LOBE IN IOWA

A distinct but open pattern is shown by solid lines, a vague pattern by dotted lines, and a distinct but crowded pattern by wavy lines.

Ames have been recognized on the Mankato drift plain, but these series do not occupy extensive areas.[4]

Soils of the Clarion series have been formed under tall grass vegetation and good natural drainage from the calcareous drift of the Mankato lobe. These soils occupy the swells on the surface of the ground moraine. The characteristic profile consists of three principal horizons which lack well-defined boundaries. The surface horizon (A), 10 to 14 inches thick, is brownish-black,[5] slightly to medium acid in reaction, and of intermediate texture. Below the surface is a

[4] Descriptions of these soils and more information about the Clarion and Webster series can be found in county soil survey reports, in *Soils of Iowa* (1), and in *Soils and Men* (6).

[5] The color names are those given by Rice et al. (5).

transitional layer (B) that is dark yellowish-brown, slightly acid to neutral in reaction, of intermediate texture, and from 5 to 22 inches thick. The third and deepest horizon (C) of the profile is the calcareous till, which begins at depths that may range from 15 to 36 inches but usually fall between 24 and 30 inches. The till ranges from weak yellow to light yellowish-brown in color and from clay loam to clay in texture.

The members of the Webster series are associated with the Clarion soils and occupy about the same aggregate area. They also have been formed from drift, but they occupy the swales or depressions and were developed under conditions of restricted natural drainage. The characteristic profile of the Webster soils has a surface layer (A) that is black, 14 to 20 inches deep, neutral to alkaline, and of intermediate to heavy texture. Below the surface horizon, the soil material grades through a dark gray layer of heavy texture (B), 6 to 10 inches thick and in many places calcareous, into the light gray, calcareous till (C). Faint mottlings of weak orange are commonly present in the light gray till, which ranges in texture from clay loam to clay. The Webster soils differ from the Clarion primarily in the thickness, color, and reaction of the A horizon and in the color of the C horizon. The Webster soils are generally heavier in texture in the surface layer, the predominant types being clay loam and silty clay loam instead of loam and silt loam as in the Clarion series.

ANNUAL RECESSIONAL MORAINES

Observations from aerial photographs

Aerial photographs of youthful drift plains generally present a mottled appearance due to alternating light and dark areas. The mottlings are without apparent arrangement in many instances, but in aerial mosaics for a number of counties of the region of the Mankato lobe in Iowa, the light and dark areas form a banded pattern. The light patches on the photographs are generally end to end, like rows of elongate rounded beads, and they have long axes, generally parallel to the margins of the drift sheet. The rows of light patches are separated by dark lenticular areas, and this gives a banded appearance to the photographs, as is shown in a section of the mosaic for Story County, Iowa, in figure 2. The bands are slightly curved with the concave side toward the interior of the lobe. The light patches represent areas as long as 600 feet on the ground, and there are approximately 15 rows of patches per mile. The light-colored bands on the photographs have been identified as low ridges or swells, whereas the dark-colored areas are depressions or swales. Locations of the more prominent swells in the area shown in figure 2 are represented in the sketch map in figure 2*a*.

The arrangement of the swells and swales in a pattern is not sufficiently definite or of sufficient relief to be apparent easily from the ground. It does not appear on the standard quadrangle maps of the U. S. Geological Survey because the contour interval of 20 feet is too large to show the small variations in relief. Once the existence of the pattern has been established, however, it can be recognized on more recent soil maps (4). The pattern is more readily apparent on aerial mosaics than on other pictures or maps available or from ground inspection.

Origin of the swale and swell pattern

The pattern of swales and swells on the Mankato lobe has been interpreted as one of annual recessional moraines (2). The interpretation of the swells as recessional moraines is based upon their shape and upon their arrangement in belts which outline what must have been successive positions of the receding ice front. During each summer, melting and recession would occur along the glacial front with resulting deposition. In each subsequent winter, readvance of the glacier would cover part of the territory freed from ice in the previous summer.

FIG. 2. AERIAL MOSAIC OF PARTS OF GRANT AND MILFORD TOWNSHIPS, STORY COUNTY, IOWA

The annual recessional moraines are the light bands that lie in a northeast-southwest direction.

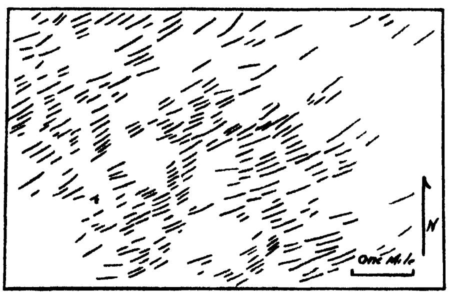

FIG. 2a. SKETCH MAP SHOWING THE DISTRIBUTION OF THE PRONOUNCED SWELLS AMONG THE MORAINES THAT APPEAR IN FIGURE 2

As the ice again melted the following year, thicker deposits would be formed in the area covered by the winter readvance of the glacier. These areas of glacial readvance and thicker deposits would thus become the swells, and the intervening areas not reoccupied by the ice would remain as swales. The swells for the most part are believed to represent the melting of single summers and hence to be annual, since otherwise they would vary more in height in accordance with the range in the numbers of summers required for their formation. The swells would be expected to be discontinuous along the front of the retreating glacier because of uneven advances and retreats of the ice and differences in glacial load. During the melting of the ice in summer, outflowing waters would carry

away silt and clay, part of which would settle out from the water collected in the swales. Such a mechanism would account in part for the general occurrence of heavier textures in the surface horizons of the soils that occupy the swales.

SOIL TYPE PATTERN AND THE ANNUAL MORAINES

The Clarion and Webster soils form a patchwork over the area of the Mankato lobe in Iowa, and the pattern has been considered entirely haphazard. Variations in glacial load from place to place have been thought to be the explanation for the variations in surface configuration and consequent soil type pattern on the drift plain. In more recent soil surveys in the area, however, the pattern of low recessional moraines is repeated partly on the soil map. An example, taken from the soil map of Story County, Iowa, to represent the area shown in the aerial mosaic in figure 2 is given in figure 3. This map was prepared on a plane-table base before aerial photographs for the county were available. Neverthe-

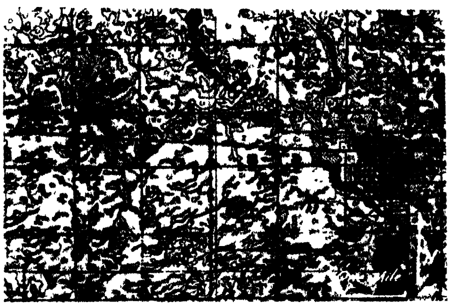

FIG 3 MAP SHOWING THE DISTRIBUTION PATTERN OF CLARION AND WEBSTER SOILS IN PARTS OF GRANT AND MILFORD TOWNSHIPS, STORY COUNTY, IOWA

Clarion soils are indicated by symbols Cl and Cf; Webster soils, by Wm and Ws.

less, the areas of soils tend to have long parallel axes in a northeast-southwest direction as do the annual recessional moraines. The pattern of soil types is banded, and the bands have the general form and arrangement of the annual recessional moraines shown on the aerial mosaics.

Wherever a pattern of low recessional moraines exists on the surface of the Mankato lobe, the Clarion soils occupy most of those moraines with the Webster soils in the intervening swales or depressions. Occasional areas of other soils occur where the drift is sandy or gravelly, but such soils are not considered here because of their comparatively limited extent. The banded patterns of Clarion and Webster soils, which prevail in regions with distinct low moraines, have the long axes of individual bands parallel to the margins of the lobe. This arrangement can be expected in a number of places on the Mankato lobe, and the identification of the pattern is readily accomplished from the study of the mosaics for county areas. Areas in which the pattern of annual recessional moraines has been identified are shown in figure 1.

The existence of low recessional moraines which affect the pattern of soil types

may extend to parts of the Wisconsin drift plain outside of Iowa and to parts of other glaciated regions in an early stage of the erosion cycle. Identification of the pattern of low moraines in regions comparable to the Mankato lobe and the establishment of the influence of that pattern on soil type distribution are comparatively easy. Additional knowledge thus made available should be helpful in the making of soil surveys, both in the classification of the soils and in the field mapping. Conversely, the relationship between the annual moraine and soil type patterns indicates a possible application of soil maps in studies of surface geology.

SUMMARY

The distribution of soil types in many parts of the Mankato lobe in Iowa is a reflection of a banded pattern of annual recessional moraines. Clarion soils, members of the prairie group, occupy the low but well-drained swells, whereas Webster soils (Wiesenboden) have been formed in the intervening swales where natural drainage was restricted. The low recessional moraines, which can be identified readily from the study of aerial mosaics, range up to 600 feet in length, with long axes tending to parallel the outer edges of the lobe. The similarity in pattern of moraines and soil types is evident from a comparison of aerial mosaics and recent soil maps for counties in north-central Iowa. The relation between soils and low moraines in north-central Iowa may exist in other glaciated regions in an early stage of the erosion cycle. Recognition of the pattern of moraines should be helpful in the mapping of soils, and conversely, the soil maps may be helpful in the study of surface geology.

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NOTES ON THE INFLUENCE OF MICROORGANISMS ON GROWTH OF SQUASH PLANTS IN WATER CULTURE WITH PARTICULAR REFERENCE TO MANGANESE NUTRITION[1]

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Hoagland, Chandler, and Stout (4) and Ark (1) have presented evidence indicating that soil microorganisms may sometimes be concerned, directly or indirectly, in the development of "little leaf" or "white bud" symptoms in annual and perennial plants grown in zinc-deficient soils or culture solutions. It was observed, for example, that after treatment with steam, formalin, or ether, many disease-producing soils supported the growth of healthy plants. Although no certainty exists that the effectiveness of these agents is due solely to their germicidal properties, still this is the simplest and most obvious explanation of their function. This interpretation is further supported by the observation that the disease-producing soil that was improved by steam sterilization commonly reverted to its original toxic condition, as judged by the poor growth of test plants, following reinoculation with 1–2 per cent by weight of disease-producing soil.[2] This observation provided the starting point for the present investigation.

An attempt was first made to repeat the inoculation experiments with sterilized soil. Without describing the experiments in detail, it may be said that the results were extremely erratic. Although in some individual experiments results were obtained completely in accord with the earlier observations, in others, no beneficial influence of sterilization or deleterious influence of inoculation could be observed. Indeed, in some experiments the reinoculated soils produced plants superior to those from the uninoculated soils.

It is not surprising that erratic results were obtained in these experiments when one considers the fact that the conditions were quite inadequate from a bacteriological point of view. The soils were steam-sterilized in crocks which, after cooling, were planted to corn, without sterile precautions. The soils in some of the crocks were reinoculated, whereas others were left uninoculated; but during the 4- to 8-week growth period both were constantly exposed to the dust of a greenhouse usually containing disease-producing soils. Consequently there could be no certainty that the microbiological populations of the inoculated and the control soils differed significantly.

[1] Clerical assistance in the preparation of this publication was furnished by the personnel of the Work Projects Administration, Official Project No. 65-1-08-911B10.

The authors express their appreciation to D. R. Hoagland for his kind suggestions in connection with this problem.

[2] The recent explanation of these effects has been based on the supposition that the microorganisms, through competition for zinc or in some other manner, depressed the absorption of zinc by the crop plants.

Because of this limitation of the soil-pot method of studying the relation of microorganisms to mineral-deficiency symptoms, it was decided to adopt a more adequate technique for further investigations. The objective was to control both the physical and the microbiological environments to which the plants would be exposed. For this purpose the water-culture technique, so modified as to protect completely the root systems of the plants from unintentional contamination with microorganisms, was used.

Some preliminary experiments with the sterile water-culture technique were carried out with corn plants and zinc-deficient solutions. Neither the plants nor the solutions, however, proved to be satisfactory for our purpose. The structure of corn and other grasses is such as to make it difficult to prevent microorganisms from passing down between the leaf sheathes of the shoot and reaching the root culture medium. The solutions were unsatisfactory because they could not readily be kept free of zinc contamination derived from the rubber tubing used to connect the flask containing the plant with a water reservoir. In view of these difficulties it was decided to substitute squash for corn as a test plant and to use manganese-deficient rather than zinc-deficient solutions. Squash seedlings have a long, smooth, sturdy stem ideally suited to the requirements of the sterile technique employed. The substitution of manganese for zinc was not in itself objectionable in view of evidence by Gerretsen (2) indicating that the onset of manganese-deficiency symptoms may also be influenced by microorganisms. The symptoms in question are a chlorosis of the mottle type with eventual necrosis of the leaves and a stunting of the roots and shoots. Manganese-deficient squash (whether grown in the presence or absence of microorganisms) does not show localized lesions such as those that have given rise to the name "gray speck disease" in oats. No difficulty was experienced in avoiding manganese contamination.

The experiments described below are concerned, then, with the influence of microorganisms on the growth of squash in manganese-deficient and in "complete" culture solutions.

MATERIAL AND METHODS

The sterile-culture technique used was very similar to that described by Hausen [see Virtanen (6)]. Hubbard squash seeds were sterilized, after removal of the seed coats, by immersion for 1 minute in 95 per cent ethyl alcohol and for 10 minutes in a 0.1 per cent $HgCl_2$ solution. During the latter treatment the container was twice evacuated to remove gas bubbles adhering to the seeds. The sterilized seeds, after washing and soaking, were transferred to individual 24- by 250-mm. test tubes containing about a 7-cm. layer of sterile 0.65 per cent agar plus 0.25 per cent peptone. It was found that seeds developed best if they were only partly immersed in the agar. The seedlings were allowed to grow in the dark until the shoot reached a length of about 8–12 cm. At this stage, vigorous, sterile specimens were transferred to the experimental vessels under aseptic conditions. Contaminated seedlings could usually be recognized by a heavy growth of microorganisms on the peptone-containing germination me-

dium. The yield of sterile and healthy seedlings suitable for subsequent experimentation varied from 25 to 90 per cent of those initially cultured in the agar-peptone medium.

The vessels used for the further growth of the seedlings consisted of a 1-liter pyrex suction flask connected to a 3-liter reserve nutrient flask by means of a short piece of rubber tubing. The suction flask was provided with a rolled cotton plug to support one seedling and to protect its roots from microbial contamination. The reserve flask was designed so that liquid could be pumped to the plant flask as required. Three and one-half liters of nutrient solution was put into the two vessels, and containers and contents were then sterilized by autoclaving. The basic nutrient solution contained, per liter of glass-distilled water, 5 ml. *M* $Ca(NO_3)_2$, 5 ml. *M* KNO_3, 2 ml. *M* $MgSO_4$, 1 ml. *M* KH_2PO_4, and 1 ml. of a solution containing 0.5 gm. $FeSO_4 \cdot 7H_2O$ plus 0.4 gm. tartaric acid per 100 ml. In addition, the following micronutrient elements were added in the concentrations indicated: B and Mn, 0.5 p.p.m.; Zn, 0.05 p.p.m.; Cu, 0.02 p.p.m.; Mo, U, Cr, Ni, Co, W, and Ti, 0.01 p.p.m. The ferrous tartrate was sterilized separately and added when the seedlings were transferred. These latter operations were carried out in a dust-free room to minimize the chances of air-borne contamination.

The plants were immediately transferred to a greenhouse and were grown until the nutrient supply in the reserve flask of the most actively growing plant was exhausted. This occurred in from 3 to 8 weeks, depending on the weather.

The plants were inoculated as required by adding 0.1–0.5 gm. fresh, normal garden soil to the plant flask. Inoculations were usually made 1–3 weeks after the plants were placed in the greenhouse. Continuous aeration, if required, was started at the time of inoculation. Sintered pyrex glass aerators were used. At the end of the growth period the root systems were examined for contamination by inoculating 1 ml. of the residual culture solution into a yeast-agar-dextrose medium incubated aerobically at 28°C. If no colonies appeared after 7 to 10 days, the roots were considered to have been sterile. The results were usually very definite, the test medium either remaining sterile or showing thousands of colonies. The percentage of sterile plants varied from 0 to 75 per cent of the total number cultured; the average was about 50 per cent.

RESULTS

Influence of microorganisms on the growth of plants with and without adequate manganese

The results of several experiments were conclusive in showing that sterile squash plants readily develop manganese-deficiency symptoms. This applied to plants grown in a solution containing a small amount of Mn (0.1 mgm. Mn per plant) as well as in Mn-free solutions ($<$ 0.01 mgm. per plant). It should be mentioned that about 1 mgm. Mn per plant was needed to allow maximum growth under the conditions of the experiments. Chance contaminants (bacteria and fungi) present on the roots of several plants appeared to exert no deleterious effect on plant development. Plants inoculated with soil, however,

were definitely inferior to sterile controls. For example, the average dry weight of the shoots of four sterile plants was 8.4 gm., whereas the average for the three soil-inoculated plants was 5.8 gm.

Since manganese-deficient plants develop more poorly when inoculated with soil, it seemed desirable to find out whether plants adequately supplied with manganese are similarly affected. Numerous experiments have shown that they are so affected and that the degree of growth inhibition is at least as great as with manganese-deficient plants. The results of a typical experiment are given in table 1.

In this experiment three treatments were applied. Besides the unaerated inoculated and unaerated sterile plants, four others were both inoculated and aerated. Twenty-one days after the differential treatments were started, the plants showed marked differences in size and general appearance. The unaerated sterile plants were generally the best, and the unaerated inoculated

TABLE 1

Growth of high-manganese squash plants in the presence and in the absence of soil microorganisms

PLANT NUMBERS	GROWTH CONDITIONS*		FINAL pH OF CULTURE SOLUTION	AVERAGE DRY WEIGHT	
	Soil inoculation	Aeration		Shoots	Roots
				gm.	*gm.*
1–4	Sterile	Nonaerated	4.6 ± 0.28	13.3 ± 2.5	2.3 ± 0.16
5–8	Inoculated	Aerated	7.3 ± 0.46	8.8 ± 3.0	1.5 ± 0.61
9–12	Inoculated	Nonaerated	8.1 ± 0.15	5.4 ± 1.5	0.88 ± 0.29

* Sixteen days after the seedlings were transferred to sterile culture flasks and placed in greenhouse, flasks 5–12 were inoculated with 0.25 gm. soil and aeration was started in flasks 5–8; the plants were harvested 21 days later. All plants were supplied with 2 mgm. Mn; initial pH 5.6.

plants were the poorest. The sterile plants were, on the average, about two and one-half times as large as the unaerated inoculated plants. Under the existing experimental conditions the growth of shoots and roots was about equally retarded by the presence of soil microorganisms.

In spite of the almost equal retardation of root and shoot growth in this and other experiments, there can be little doubt that microorganisms influence the plants primarily through their action upon the roots. This follows almost directly from the nature of the inoculation technique and is also fully supported by observations on the changes in the appearance of the root systems and the nutrient solutions. Within a few days after inoculation, the nutrient solutions, previously clear, become turbid, and the roots invariably lose a conspicuous part of their turgor and change from an almost pure white to a light yellowish-brown (fig. 1). Both these changes suggest a loss of vitality. Daily observations of inoculated plants give the impression that only after these root effects appear does shoot growth begin to be retarded.

In one experiment in which plants were inoculated with pure cultures of

bacteria isolated from heavily contaminated, soil-inoculated roots, some root injury was observed. The experiments so far undertaken with pure cultures have, however, given such variable results that no generalizations can be made. Nevertheless, attention should be drawn to the possibility that the injurious effects of soil inoculation are due to the activities of a relatively few types of microorganisms which are specially adapted to living on root surfaces.

The results of the experiments thus far presented indicate that squash plants

FIG. 1. CHANGES IN THE ROOT SYSTEMS OF SQUASH FOLLOWING INOCULATION WITH 0.5 GM. OF NORMAL GARDEN SOIL

A, inoculated 2 weeks before harvesting; B, inoculated 1 week before harvesting; C, uninoculated control. All plants were grown for 27 days after being transferred to sterile culture flasks. Differences in shoot size are probably not significant.

produce completely healthy roots (under the chosen experimental conditions) only in the absence of heavy microbial contamination such as results from inoculation with soil.

Influence of microorganisms on oxygen requirements and root respiration

The question now arises as to how microorganisms exert their injurious effect. At the outset it must be emphasized that no evidence has been obtained in favor of the view the microorganisms act by invading the living root cells. Although

this possibility cannot at present be excluded, the experiments to be described indicate that at least a part of their influence is exerted by indirect means.

A striking feature of the growth of squash in the absence of microorganisms is the large size and excellent condition of the roots that develop in a small volume (400–500 ml.) of "complete" nutrient solution. Plants grown in ordinary nonsterile solution cultures develop comparable root systems, even in a much larger volume of solution, only when extra aeration is provided. This suggested that the injury resulting from inoculation may be due to oxygen deficiency.

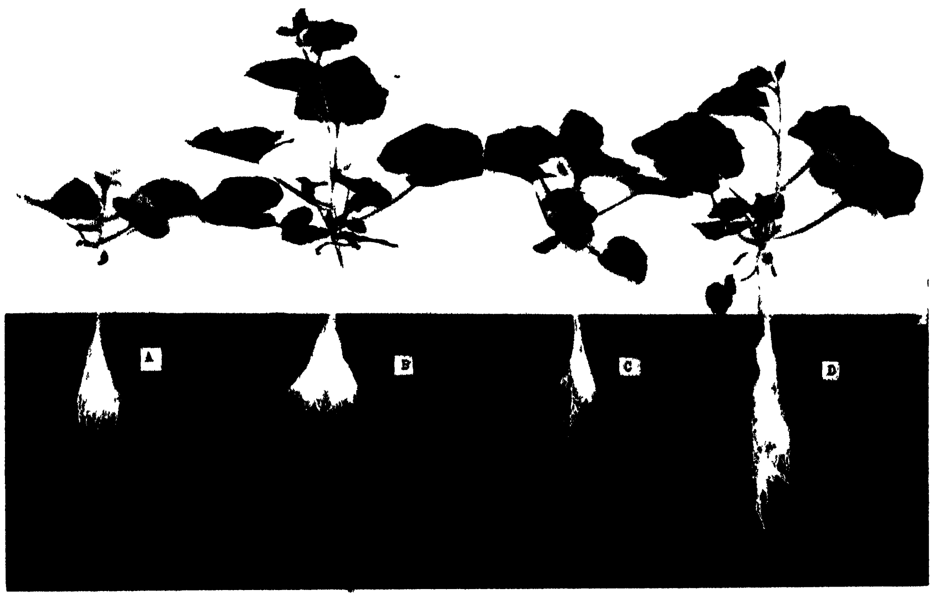

FIG. 2. EFFECTS OF INOCULATION, AERATION, AND Mn SUPPLY ON THE GROWTH OF SQUASH

A, minus Mn, sterile. Plants B, C, and D are provided with a "complete" low-Mn (0.2 mgm. Mn per plant) nutrient solution. B, sterile; C, inoculated with 0.1 gm. soil, 10 days earlier, nonaerated; D, inoculated and aerated. All plants were grown for 21 days after being transplanted.

If the above deduction were correct, one would expect that injury to soil-inoculated plants could be reduced by improving the oxygen supply of the roots. Some evidence that this can be done has already been presented in table 1. Similar and always consistent results have been obtained in several experiments. Figure 2 shows typical plants from one such experiment. It can be seen that the inoculated and aerated plant is much superior to the inoculated and unaerated plant, but even the aerated plant is not so vigorous as the unaerated sterile control supplied with the same amount of manganese. It has been generally observed that although aeration improves the growth of inoculated plants it does not entirely prevent root injury. This would seem to indicate that oxygen deficiency is not the only, and perhaps not even an important, cause of root injury.

Figure 2 provides additional evidence pointing to the same conclusion. It can be observed that the sterile root systems of plants A and B are almost the shape of the suction flasks in which the roots were enclosed and that there is a very heavy growth of secondary roots and root hairs in the part that was above the nutrient solution (upper two-thirds), whereas the lower part is composed of short, coarse, and slightly branched roots. The failure of the latter to elongate farther can be interpreted with some confidence to mean that the nutrient solutions even of the sterile plants were not adequately supplied with oxygen. But this deficiency was evidently of no importance for these plants, in view of the excellent condition of the upper part of the root system.

The foregoing observations lead to the conclusion that the injury resulting from heavy contamination is not due primarily to oxygen deficiency but is the

TABLE 2

Influence of microorganisms and aeration on subsequent respiration of excised squash roots

EXPERIMENT	GROWTH CONDITIONS			NUMBER OF PLANTS	FRESH WEIGHT OF ROOTS*	RESPIRATION RATE	
	Inoculation	Mn	Aeration			CO_2/hr./plant	CO_2/hr./gm. fresh wt.
					gm.	*mgm.*	*mgm.*
A†	Sterile	+	Nonaerated	3	37.4 ± 5.7	8.51 ± 1.7	0.23 ± 0.05
	Inoculated (1 week)	+	Nonaerated	4	37.2 ± 5 4	12.6 ± 1.7	0.34 ± 0.06
	Inoculated (2 weeks)	+	Nonaerated	4	21.0 ± 5.1	11.2 ± 2.7	0.56 ± 0.18
B	Sterile	–	Nonaerated	2	8.45 ± 0.63	0.680 ± 0.02	0.082 ± 0.01
	Sterile	+	Nonaerated	4	38.3 ± 7.5	3.20 ± 0.36	0.083 ± 0.00
	Inoculated (3 weeks)	+	Aerated	3	25.0 ± 4.7	3.91 ± 0.30	0.159 ± 0.02
	Inoculated (3 weeks)	+	Nonaerated	3	19.1 ± 2.1	4.32 ± 0.82	0.207 ± 0.00

* The fresh weights of the roots were obtained after standardized centrifugation.

† The plants used in experiment A are the same as those shown in figure 1.

All data represent averages for the indicated numbers of plants.

result, at least in part, of injury to those parts of the root system situated above the solution level. The mechanism of this growth inhibition is not yet clear. Possibly a whole complex of factors is involved.

Although the inferior growth of inoculated plants may not be attributed primarily to oxygen deficiency, it nevertheless seemed worth while to determine whether or not the respiratory rate of the root system is increased by the presence of microorganisms. Several experiments were consequently carried out by a previously described excised-root technique (3). Before use, the roots were always thoroughly washed in running water to remove all but the most firmly adhering microorganisms. The respiratory measurements were carried out at 25°C. over an interval of 2 to 4 hours. Data from two typical experiments are given in table 2.

The data show that the rate of carbon dioxide production per unit fresh weight of heavily contaminated roots is considerably greater (132 to 250 per cent) than

that of sterile control roots. The respiratory rate of the excised roots appears to increase with the time elapsing between inoculation and harvesting (experiment A). Aeration of the roots during the growth period partly prevents the respiratory increase due to heavy contamination just as it prevents visible injury to the roots.

Attention should be directed to the fact that the observed respiration is not the result of the metabolic activity of the plant roots alone, but is due to the roots plus the associated microorganisms. It is not possible, however, to decide what part of the total respiration is contributed by the individual components of the plant-microbe system. The large increase in respiration resulting from inoculation may be produced by the roots alone, by the microorganisms alone, or by both.

The importance of the observed differences in respiratory rates between inoculated and sterile roots with respect to the growth phenomena described above is difficult to evaluate. A definite possibility exists that the increased respiratory activity of contaminated plants does diminish the oxygen supply sufficiently to affect adversely root development. Before any definite conclusion can be reached on this point it will be necessary to study the relation of root development to oxygen tension and also to determine the actual oxygen tensions existing in the nutrient solutions of sterile and of heavily contaminated cultures.

pH changes and iron requirements in sterile and inoculated cultures

Another difference between sterile and inoculated cultures that may possibly be of significance in explaining the injurious action of microorganisms on the plants is the change in pH of the medium occurring during plant growth. When plants are grown in ordinary nonsterile nutrient solutions, the pH almost invariably increases as growth proceeds. This behavior is commonly attributed to a more rapid absorption of anions than cations. It would be expected that soil-inoculated squash plants would also cause an alkaline shift, and this is actually found to be so. With sterile plants, on the contrary, there is no tendency for the pH to increase. The pH may remain approximately constant, but more commonly it drops significantly,[3] sometimes as low as pH 3.5. Some data illustrating this phenomenon have already been presented in table 1, and a further example is given in table 3.

What effect will the high acidity have on the growth of sterile plants? Acidities in the range here involved appear not to be injurious to squash[4]; healthy plants have been obtained in solutions as acid as pH 3.1. The low pH may actually be beneficial by virtue of its influence in increasing the solubility of iron.

In this connection it is significant that the iron requirement of sterile plants

[3] The pH of the culture medium may also decrease when squash plants are grown under ordinary water-culture conditions.

[4] It should be noted that the continued growth of plants at the relatively high acidities found in the body of the nonstirred media probably represents adaptation of the root organ to its environment.

is extraordinarily low: 1–1.5 ml. of the iron tartrate solution per liter of nutrient solution is sufficient to satisfy the iron requirements of a single squash plant for the entire period of growth in these experiments (3–8 weeks). Heavily contaminated plants, on the contrary, may show iron chlorosis and respond to further additions of iron tartrate. The more efficient utilization of iron in sterile cultures is doubtless due not only to the higher acidity but more particularly to the absence of microorganisms that destroy the iron tartrate complex by decomposing the organic radical.

Anaerobic carbon dioxide production by sterile squash roots

The relative rates of aerobic and anaerobic carbon dioxide production by plant roots have been the subject of several earlier investigations in this laboratory by Hoagland and Broyer (3) and by Ulrich (5). The interpretation of the data, however, has always been uncertain because nonsterile roots were used and, consequently, the relative importance of the two components of the plant-microbe system could not be accurately evaluated. The rates of aerobic and anaerobic carbon dioxide production by sterile roots were measured, therefore, to find out how the metabolism of the plant alone is influenced by the oxygen supply, and at the same time the respiration of nonsterile squash roots was observed under comparable conditions.

TABLE 3

*pH changes in sterile and in inoculated cultures of squash plants**

GROWTH CONDITIONS		pH AFTER VARIOUS PERIODS OF GROWTH			
Inoculation	Aeration	0 days	12 days	19 days	22 days
Sterile	Nonaerated	5.8	...†	. †	3.9
Inoculated	Nonaerated	5.8	4.6	5.3	5.7
Inoculated	Aerated	5.8	5.1	5.7	5.8

* All plants were grown in a complete nutritent solution. The pH values represent averages for three cultures. Note that the inoculations were carried out on the twelfth day.

† To avoid contamination, pH determinations were made on these cultures only at the beginning and at the end of the experiment.

The roots of plants grown under sterile or nonsterile conditions were excised and thoroughly washed in distilled water. They were then immersed in a solution of 0.005 N $CaSO_4$ in a flask maintained at 25°C., and the aerobic and anaerobic carbon dioxide production was measured during successive 5-hour periods. During the aerobic period, CO_2-free air was passed through the bathing medium at the rate of about 10 liters per hour; the respired carbon dioxide was collected in 0.01 M $Ba(OH)_2$ and estimated conductimetrically. During the following anaerobic period CO_2- and O_2-free nitrogen was passed through the bathing medium. The summarized data of one experiment are presented in table 4.

The data show that sterile, like nonsterile, roots produced carbon dioxide in the absence as well as in the presence of oxygen. In all instances, the rate of anaerobic carbon dioxide formation is considerably lower than the aerobic rate. With sterile roots the anaerobic rate is about one third that of the aerobic rate;[5] with the nonsterile roots this ratio is almost 1 to 2. Although the sterile and the nonsterile roots do not respond in exactly the same way to changes in the oxygen supply, nevertheless their behavior is sufficiently alike to justify the belief that the anaerobic carbon dioxide production of nonsterile roots under the existing conditions is largely due to the plant component of the root-microbe system. This is in agreement with earlier conclusions based on more indirect evidence.

TABLE 4

*Influence of microorganisms on aerobic and anaerobic respiration of excised squash roots**

PLANT NUMBER	Mn	INOCULATION	FRESH WEIGHTS OF ROOTS	RESPIRATION RATE, CO_2 PER HOUR PER GRAM FRESH WEIGHT		RATIO OF ANAEROBIC TO AEROBIC RESPIRATION RATE (AVERAGE)
				Period 1, aerobic	Period 2, anaerobic	
			gm.	*mgm.*	*mgm.*	*per cent*
1	+	Nonsterile	13.0	0.458	0.232	
2	+	Nonsterile	21.0	0.640	0.347	46
3	−	Nonsterile	4.1	0.305	0.068	
4	−	Sterile	8.8	0.174	0.045	
5	+	Sterile	39.8	0.225	0.099	36
6	+	Sterile	22.2	0.333	0.118	

* The sterile plants were grown for 39 days by the described sterile-culture technique, whereas the nonsterile plants were grown for 33 days in beakers by the more usual solution-culture technique. Because of these differences of treatment, the absolute rates of respiration of sterile and nonsterile plants are not directly comparable.

SUMMARY

Squash plants grown in manganese-deficient culture solutions show typical deficiency symptoms whether or not the roots are sterile.

Heavily contaminated, soil-inoculated plants are generally smaller and less healthy than plants with sterile root systems. This applies to plants grown in "complete" nutrient solutions as well as in manganese-deficient solutions. The influence of microorganisms is first manifested by root injury, but very soon the whole plant is affected. The relation of these phenomena to the micronutrient deficiency symptoms of plants growing on certain disease-producing soils is not yet clear.

Heavily contaminated excised roots have a consistently higher respiratory rate than comparable sterile roots. The relative oxygen deficiency that may result under certain conditions from the greater oxygen consumption of con-

[5] This is approximately the relation found in the earlier barley root experiments of Hoagland and Broyer (3) in which there was no inoculation of the solution and the activity of microorganisms was probably low during the limited periods of the experiments.

taminated roots may play a part in root injury. Other undefined factors, however, are probably more important.

The apparent iron requirements of sterile plants are smaller than those of heavily contaminated plants. This is probably due to two factors: first, the pH of culture solutions in which sterile plants are grown tends to be lowered rather than raised as with contaminated plants; second, the organic radical of the iron salt is not decomposed.

Excised sterile squash roots produce about one third as much carbon dioxide anaerobically as aerobically. The comparative behavior of sterile and contaminated roots indicates that carbon dioxide produced anaerobically by the latter is largely due to the plant component of the plant-microbe system.

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ARE THERE OBLIGATE CELLULOSE-DECOMPOSING BACTERIA?

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The claim has often been made that certain bacteria which decompose cellulose—notably spore-forming anaerobes, some of the *Cellvibrio* and *Cellfalcicula* species, and the soil *Cytophaga* group—are unable to utilize any other carbon source, even cellobiose and dextrose. In the case of the anaerobic forms there are conflicting observations on this point, and the whole question has been obscured by the difficulty of obtaining pure cultures.[1] The claims for obligate cellulose decomposition by *Cellvibrio* and *Cellfalcicula* species rest on one piece of work.[2] The case for the cytophagas, however, has long been regarded as unassailable; none of the numerous workers with these forms[3] has ever reported growth in a medium devoid of cellulose. Furthermore, it has been shown[4] that dextrose and other reducing sugars when present in a concentration as low as 0.1 per cent completely inhibit growth and cellulose decomposition. My own studies on these organisms[5] at first fully substantiated both points. Thus the biochemical anomaly of organisms attacking a polysaccharide but unable to attack its constituent disaccharides and monosaccharides seemed firmly established.

The initial indication that there might be a fallacy in this conclusion came from a manometric experiment, designed to test the effect of dextrose and cellobiose on the respiration of *Cytophaga hutchinsoni*, which yielded the rather unexpected result that these two sugars were oxidized at the same rate as cellulose. Since it appeared improbable that substances which could be oxidized so readily should be not only unutilizable but toxic in growth experiments, the previous work was critically examined for possible flaws. In all my growth experiments the sugars had been heat-sterilized together with the mineral constituents of the medium. Such a method of sterilization has long been known to cause some decomposition of reducing sugars, especially in the presence of phosphates, and although the products formed are not generally regarded as toxic to bacteria, the effect of heat-sterilization seemed the most likely cause of the discrepancies. A repetition of the growth experiments using dextrose sterilized by filtration showed that the three species *Sporocytophaga myxococcoides*, *Cytophaga hutchinsoni*, and *C. rubra* all grew excellently in a mineral medium with filtered dextrose as the sole carbon

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1 Cf. R. Meyer, *Arch. Mikrobiol.* 5: 185, 1934, for a discussion.

2 S. Winogradsky, *Ann. Inst. Pasteur* 43: 549, 1929.

3 Winogradsky, *ibid.*; H. B. Hutchinson and J. Clayton, *Jour. Agr. Sci.* 9: 143, 1919; C. Stapp and H. Bortels, *Zentbl. Bakt.* (II) 90: 28, 1934; A. Imsenecki and L. Solntseva, *Bul. Acad. Sci. U. R. S. S., Biol. Ser.*, 6: 1115, 1936; E. Walker and F. E. Warren, *Biochem. Jour.* 32: 31, 1938; H. L. Jensen, *Proc. Linn. Soc. N. S. Wales* 65: 543, 1940.

4 Hutchinson and Clayton, *ibid.*; Imsenecki and Solntseva, *ibid.*

5 Unpublished.

source in quantities ranging from 0.1 to 0.5 per cent. The filtered dextrose did not exert a "toxic effect" on growth in the presence of cellulose, although with the higher concentrations of dextrose, attack on the cellulose was diminished, doubtless because of preferential utilization of the monosaccharide as evidenced by abundant growth in the liquid. Thus the "obligate" nature of the cellulose decomposition by these organisms is simply a technical artifact. This may well prove to be the case for the other cellulose-decomposing groups for which similar claims have been made.

It seems unnecessary any longer to postulate, as did Winogradsky,[6] that there is a direct oxidation of the cellulose molecule; on the contrary, the similarity in the rates of cellulose, cellobiose, and dextrose oxidation by *C. hutchinsoni* provides good reason to believe that cellulose is decomposed by an initial breakdown to, and subsequent oxidation of, the constituent monosaccharide.

[6] Ibid.

PLANT NUTRITION AND THE HYDROGEN ION: II. POTATO SCAB[1]

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Consideration of soil acidity in terms of the entrance of hydrogen into the clay complex of the soil rather than in terms of the exit therefrom by the nutrient cations has delayed significantly the appreciation of the seriousness of our declining soil fertility. Shortages of nutrients in the soil may result in plant starvation long before anatomical symptoms indicating such irregularities are recognizable. That such fertility decline may bear some relation to potato scab, and that this disease may in no small measure be a nutrient irregularity invoking the attack by the microorganisms have seemed probable. The following study of the hydrogen ion, along with the calcium and the potassium, as factors in the incidence of potato scab may move us to consider the possibility of reducing disease incidence by undergirding the plant nutrient supply in the form of soil treatments.

PLAN OF EXPERIMENT

Chemical analyses of the crop do not constitute a code of instruction for the rate of application of fertilizers, but the chemical content of the crop *in toto* tells us what kind and how much of the fertility were mobilized out of the soil. Analyses of potato tubers impress one immediately with their high content of potassium, particularly when this is so readily associated with its role in the production and translocation of carbohydrates within the plants. Insufficient attention has been given, the authors believe, to the chemical analyses of the tops of potato plants. Unnoticed has gone the fact that these are extremely rich in calcium and that they remove large amounts of this nutrient in the crop (10 per cent ash in the tops and 25 per cent of the ash as CaO are not uncommon analyses). The composition of the potato crop as a whole, top and tubers combined, points to the demand by this crop not only for relatively large amounts of potassium per acre, but also for correspondingly large amounts of calcium as well. Recent studies (1, 4) demonstrated that the delivery of calcium by soils was declining to the extent of detriment to crop quality and yield, as well as increased incidence of what is commonly diagnosed as disease rather than plant starvation. This discovery led to the belief that to the nutritionist potato scab may suggest a disturbed calcium-potassium relation in the nutrients offered.

It was in the test of this belief that soils were prepared by means of the colloidal clay technique (2, 3) for controlling the exchangeable nutrients given the plants. In one series the supply of calcium was varied and that of potassium was held constant, and *vice versa*, both at pH 5.5, which is the reaction commonly

[1] Contribution from the departments of horticulture and soils, Missouri Agricultural Experiment Station, Journal Series No. 794.

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believed to be requisite for the inhibition of potato scab. In another series, soils were prepared with a constant potassium supply and a variable calcium offering, in one case, with the soils acid, or at a low pH of 5.2, and, in another, with the soils neutral, or at a high pH of 6.8. When calcium was held constant, the amount chosen was in relation to the amounts of phosphorus, magnesium, and other nutrients, which were held constant throughout all trials. The amount of potassium, when held constant, was similarly chosen in relation to the other nutrients or to a constant figure. The other conditions of the experiment were maintained at the usual constancy attainable.

In order to assure the presence of the scab fungus, each plant series was well inoculated with suspensions of eight strains of the potato scab organism supplied by Schaal and by Goss.[3] Replicate plants of the Warba potato variety were grown from March to May, and the harvests of five or six plants grown individually were combined to represent the crop per soil treatment.

RESULTS

Crop yields and scab incidence

That the yields of the potatoes, both tubers and tops, are correlated with the levels of calcium, as well as those of potassium, offered is clearly shown in table 1. On this acid soil at a pH of 5.5 and with constant offerings of 50 m.e. of potassium and additions of 0, 60, and 100 m.e. of calcium to that already in the natural clay, the yields of fresh tubers, the dry weights of tops, and the total dry weights of tubers and tops combined increased as larger amounts of calcium were supplied. When the calcium was constant at 60 m.e. and the additions of potassium were 10, 50, and 100 m.e., the yield increases as fresh tubers, dry tops, and total crop weights were not consistent with the increased allotments of potassium. The heaviest application reduced the potato crop.

When the incidence of scab is related to the nutrients offered, it is most significant to note that giving either liberal amounts of potassium as contrasted to calcium or generous amounts of calcium in contrast to potassium brought about decided scabbiness. Excess potassium gave more scabbiness than did excess calcium. This suggests that the practice of potassium fertilization for yield increase may be at the same time encouraging potato scab through neglect of balancing this treatment with calcium. It is significant that an increase in yield was obtained without increase in the scab incidence per unit weight of tuber produced when there was a close similarity in the amounts of exchangeable calcium and potassium added to the soil (columns 1 and 2). With a dominance of the calcium over the potassium (column 3) the yield was greater, but the relative scab incidence also was greater. The scab incidence relative to yield was lower, however, than when potassium was dominant over calcium (column 6). Excessive calcium with very low potassium (column 4) likewise is less scab-

[3] Acknowledgement is gratefully made to L. A. Schaal, associate pathologist, U. S. Department of Agriculture, Greeley, Colorado, and to R. W. Goss, professor of plant pathology, University of Nebraska.

TABLE 1

Potato crop yields and scab incidence at pH 5.5 with variable levels of exchangeable calcium and potassium

Column number		Variable calcium constant potassium			Constant calcium variable potassium		
		1	2	3	4	5	6
Calcium added	*m.e.**	0	60	100	60	60	60
Potassium added	*m.e.*	50	50	50	10	50	100
Tubers, fresh weight	*gm*	925	1313	1459	780	1313	1073
Tops, dry weight	*gm*	33.9	46.5	56.4	29.2	46.5	44.1
Tubers, dry weight	*gm.*	147.4	233.9	254.9	137.5	233.9	175.2
Total crop, dry weight	*gm.*	181.3	280.4	311.3	166.7	280.4	219.3
Number of scabby areas		14	20†	51	9	20†	84‡
Number of deep lesions		3	10	36	5	10	70

* Additions of other nutrients, P = 60, N = 60, S = 6, Mg = 6 m.e. per plant.

† In addition, one potato had 33 per cent of its surface covered with deep lesions.

‡ In addition, two potatoes were entirely covered by deep lesions.

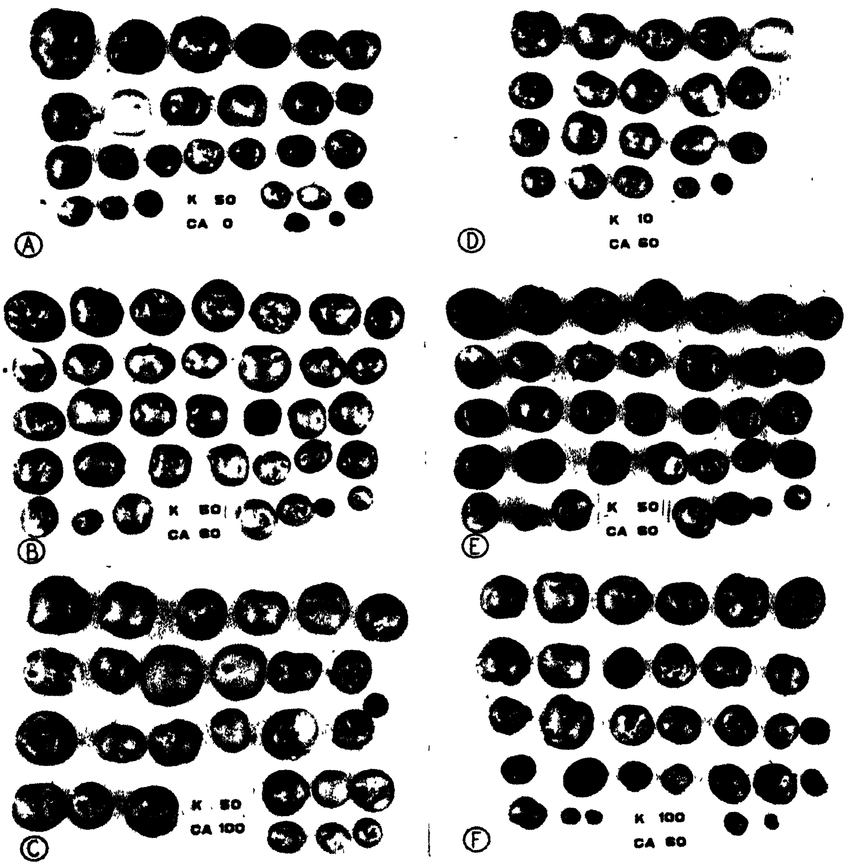


FIG. 1. POTATO YIELDS AND SCABBINESS AS RELATED TO AMOUNTS OF EXCHANGEABLE CALCIUM AND POTASSIUM ADDED TO THE SOIL

A, B, C—0, 60, 100 m.e. of calcium, each with 50 m.e. of potassium. D, E, F—10, 50, 100 m.e. of potassium, each with 60 m.e. of calcium. The 6-inch rulers are shown to indicate comparative sizes

provoking than excessive potassium over calcium, but with the former treatment only a very low yield was produced.

The differences in crop yields can be seen in figure 1, where the more uniform crop, the larger yields, and the least scabbiness are shown in B and E, given 50 m.e. of potassium and 60 m.e. of calcium. In F, with the highest potassium addition, the excessive scabbiness is readily discernible. This combination of potassium at 100 m.e. and calcium at 60 m.e. induced more scab than did that of calcium at 100 m.e. and potassium at 50 m.e. (fig. 1 C), even though the pH in both cases was at 5.5.

These data on soils at pH 5.5 demonstrate forcefully that potato scab is not entirely a matter of variety and virulence of the infecting organisms, or necessarily of variety of potato, but is also a matter of proper plant nourishment in

TABLE 2

Potato crop yields and scab incidence with constant potassium and variable calcium levels at both low and high pH values

CALCIUM ADDED / POTASSIUM ADDED	m.e. / m.e.	30 / 60		60 / 60		90 / 60	
pH values		Low	High	Low	High	Low	High
Column number		1	2	3	4	5	6
Tubers, fresh weight	gm.	1270	1120	1287	1170	1189	1042
Tops, dry weight	gm.	57.9	43.8	58.3	46.5	58.3	45.2
Tubers, dry weight	gm.	224.2	181.0	199.5	191.9	197.8	170.0
Total crop, dry weight	gm.	282.1	224.8	257.8	238.4	256.1	215.2
Number of scabby areas		42	41	6	8	19	46*
Number of deep lesions		27	21	2	6†	8‡	38

* In addition, one potato had 50 per cent of its surface covered by deep lesions.

† In addition, two potatoes each had one-fourth of the surface covered by deep lesions.

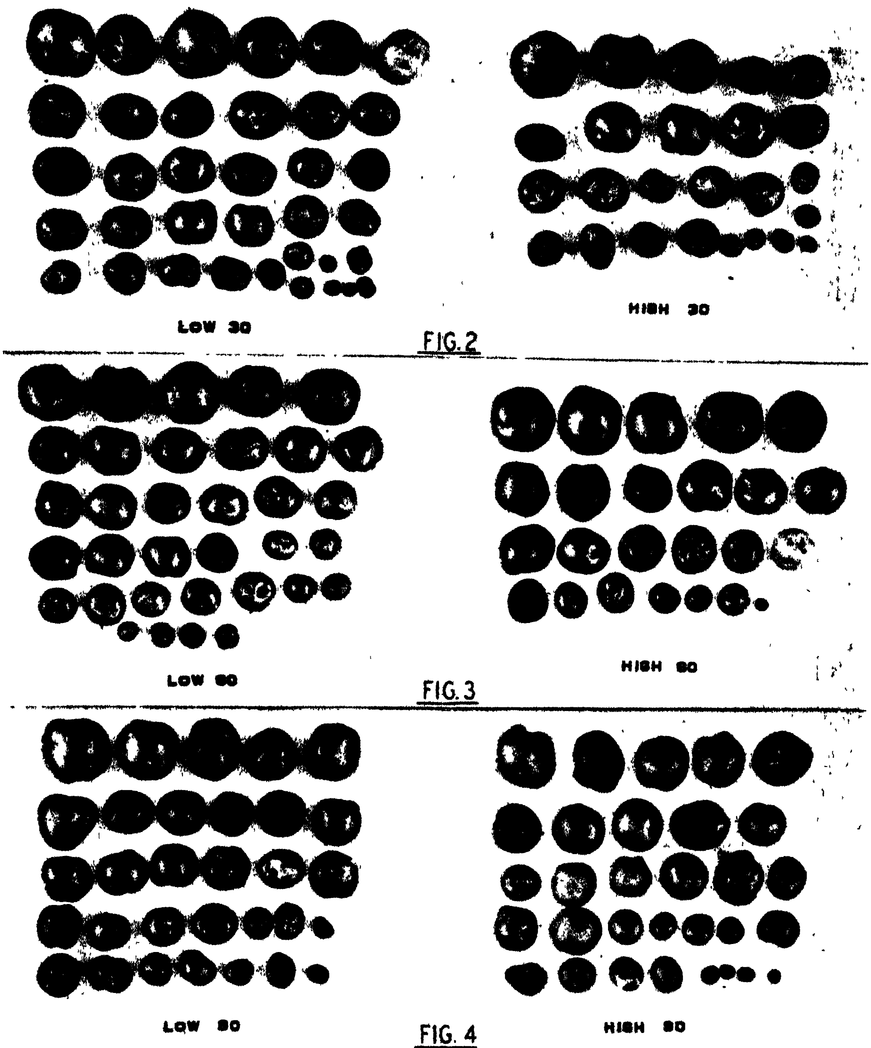
‡ Three of these lesions were on a single small potato.

terms of the fertility of the soil. They suggest, further, that in addition to calcium, other nutrients, as accompaniments to potassium and in proper relation to it, must be included for proper plant nutrition as an approach to scab exclusion.

In the attempt to segregate the significance of pH in the second series of trials, the soils of more acid reaction produced the larger yields at all nutrient levels, as shown in table 2. The increased yields of fresh tubers from the three soils of low pH over the three soils of high pH amount to 11, 9, and 12 per cent, as attributable purely to the higher degree of acidity of the soil.

It is evident that the incidence of potato scab is not directly related to the soil acidity. The number of scab areas is lowest in both acid and neutral soils when the levels of the calcium and potassium are not in distorted ratios and are in amounts similar to those effective in scab reduction in the acid soil trials of table 1. Quite contrary to the common belief in the dangers of liming for potatoes, the results show that a liberal calcium supply is not necessarily scab-

provoking. They show that calcium must be delivered, but in an acid soil rather than in a neutral soil for greater efficiency, as the figures in columns 5 and 6 of table 2 testify. An acid soil with a low supply of calcium encourages scabbiness as well as does a neutral soil, as the figures in columns 1 and 2 in the table



FIGS. 2-4. POTATO YIELDS AND SCABBINESS AS RELATED TO 60 M.E. OF EXCHANGEABLE POTASSIUM WITH 30, 60, AND 100 M.E. OF CALCIUM, AT LOW AND HIGH pH FIGURES

demonstrate in comparison with those in column 5. Increased attack by scab organisms and reduced crop yield, quite out of accord with some past concepts, may both be a result of calcium deficiency in the soil. Since the hydrogen ion serves to make some of the exchangeable nutrients of the soil more effective

(5), soil acidity in connection with scab inhibition may be playing its role merely in helping to deliver more nutrients and thus producing healthier plants through which infection is reduced. That the yield was greater at the lower pH 5.2 than at the high pH 6.8, regardless of whether the calcium applied was 30, 60, or 90 m.e. in combination with 60 m.e. of potassium, is evident from figures 2, 3, and 4. That the scabbiness is lowest at 60 m.e. of calcium, whether the pH is low or high, is shown in figure 3. This points to the significance of the fertility of the soil more than to its reaction as a scab preventive. That a neutral soil with deficient calcium encourages scabbiness as does one with similar reaction and extra calcium is shown by contrasting figures 2 and 4.

Soil fertility levels as reflected by composition of the potato tops

When the chemical contents of the potato tops grown at pH 5.5 are examined with reference to calcium and potassium in terms of both concentrations and totals, as given in table 3, some significant facts are evident.

TABLE 3

*Concentrations and totals of calcium and potassium in the tops of potato plants as related to variable levels of these two plant nutrients in exchangeable form in soil at pH 5.5**

CALCIUM ADDED	*m.e.*	0	60	100	60	60	60
POTASSIUM ADDED	*m.e.*	50	50	50	10	50	100
Column number		1	2	3	4	5	6
Calcium	*per cent*	2.38	2.15	2.26	3.06	2.15	2.03
	mgm.	807	1003	1277	896	1003	895
Potassium	*per cent*	2.96	2.92	3.33	2.18	2.92	3.38
	mgm.	1001	1358	1879	637	1358	1493

* The authors are indebted to Victor N. Lambeth for his help in this study, more particularly for the chemical analyses.

With the supply of added potassium held constant while the calcium was increased to give increased yields (table 1), there were scarcely significant differences in the calcium concentrations of the tops. For the total calcium carried by the tops, however, the figures increased as more calcium was added to the soil, with a range from 807 mgm. to a figure more than 50 per cent greater. This increased calcium removal from the soil was paralleled by increased yield in both tops and tubers.

When the supply of added calcium was constant while that of potassium was increased to give a rise and then a decline in yields, the concentration of calcium in the tops declined with successive potassium increments. The lowest calcium concentration in this series of three was not much below any of those in the series where calcium was varied. The highest concentration, 3.06 per cent, of calcium in the entire table occurs where the least amount of potassium was offered the plants, though the tops were not so vigorous as were those with the other treatments. It is particularly significant to note that potato tops contain

more than 2 per cent of calcium or the equivalent and more than is common in such legume hays as red clover. In terms of the crop of potato tops we may well think of its high need for calcium as we do for the crop of red clover.

In the series in which added calcium was constant, the total calcium taken by the tops was not consistently related to the increasing potassium applied. The maximum total calcium was in the crop with 50 m.e. of potassium rather than with the 100 m.e. This suggests that the excess of potassium is suppressing the total calcium in the tops. This lower total calcium is due to both reduced concentration of calcium and reduced yield of tops in connection with the heavier application of potassium.

The contents of potassium in the tops with variable calcium offerings were similar to their contents of calcium. The concentration was relatively constant for the three levels of calcium, but the total potassium increased as more calcium was available in the soil. When variable potassium was offered, the concentration of this nutrient increased to a figure more than 50 per cent above the lowest one, while the total potassium increased from 637 mgm. to a figure greater by more than 100 per cent. But even this seemingly large figure for total potassium taken from the soil where 100 m.e. of this nutrient was applied in connection with 60 m.e. of calcium was not so large as that taken where only 50 m.e. were applied in conjunction with 100 m.e. of calcium.

TABLE 4

Concentrations and totals of calcium and potassium in the tops of potato plants as related to variable levels of these two plant nutrients in exchangeable form in a soil at low pH 5.2 and in another at high pH 6.8

Calcium Added	m.e.	30		60		90	
Potassium Added	m.e.	60		60		60	
pH values		Low	High	Low	High	Low	High
Column number		1	2	3	4	5	6
Calcium	per cent	1.45	1.42	1.74	1.69	1.80	1.76
	mgm.	840	622	1012	787	1052	798
Potassium	per cent	3.29	3.68	3.82	3.85	4.60	3.98
	mgm.	1907	1611	2227	1790	2683	1799

These facts become evident when columns 6 and 3 in table 3 are compared with column 5. When these three calcium and potassium applications are considered it is well to note that increasing the applied calcium in conjunction with a moderate amount of potassium was more effective in bringing potassium into the tops than was doubling the potassium application in connection with a moderate calcium application.

As given in table 4, the concentration of calcium in the tops grown at pH 6.8 is but slightly lower than that in the tops grown at pH 5.2, but increases for either pH with the increments of calcium applied. Much more noticeably, the total calcium in the tops is lower as the pH figure represents more nearly neu-

trality, but in all three cases of this latter reaction the figures for total calcium are lower than the lowest in the more acid soil condition. Again at either pH figure the total calcium increased with the increments of applied calcium. The potassium in the tops, on a percentage basis, increased with increments of calcium applied, regardless of the pH. The largest figure for total potassium at pH 6.8, however, was about 6 per cent less than the smallest figure at pH 5.2.

At the reaction of 5.5 in table 3, it was shown that with greater amounts of potassium were associated increasing applications of calcium which delivered more of this nutrient. Again in table 4, the increasing calcium offered was apparently instrumental in bringing larger potassium totals into the tops. Then again, as the lower pH figure delivered more calcium than did the higher pH, so correspondingly this greater calcium delivery represented greater potassium delivery in the tops. Thus, whether by greater applications of exchangeable calcium, or merely by more calcium mobilization through the hydrogen ion associated with it (5), greater movement of calcium into the tops brought correspondingly more potassium with it. Thus, rather than an "antagonistic" effect of the calcium on the potassium, there is apparently a "synergistic" effect, in that the calcium is associated with movement of potassium into the tops. The reverse effect, or less calcium as more potassium is applied, has already been suggested in the comparisons of columns 5 and 6 with 3 in table 3. That these soils should demonstrate effectiveness of calcium in moving potassium into the potato tops in relation to yield values of tops and tubers is contrary to some past concepts.

SUMMARY AND CONCLUSIONS

The results in terms of yields of potato tubers, potato tops, and incidence of potato scab where the levels of exchangeable calcium and potassium were varied in relation to each other while other nutrients were held constant, all at different degrees of soil acidity, point to the importance of the relation of calcium to potassium in the production of this crop. Soil acidity as a means of reducing the incidence of potato scab is apparently effective because of the increased mobilization of certain cationic plant nutrients by the presence of the hydrogen ion.

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